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A-Level
Chemistry

Exam Board: OCR A

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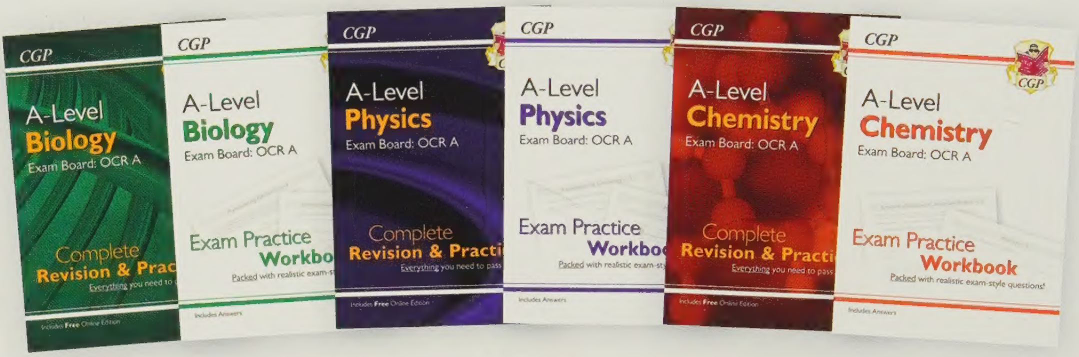
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How to use this book

Learning Objectives

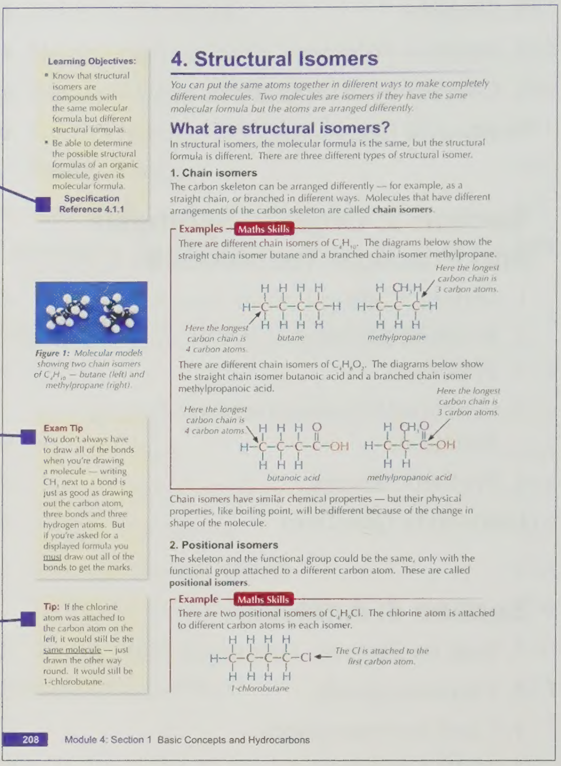
- These tell you exactly what you need to learn, or be able to do, for the exam.
- There's a specification reference at the bottom that links to the OCR A specification.

Exam Tips

There are tips throughout the book to help with all sorts of things to do with answering exam questions.

Tips

These are here to help you understand the theory.



Learning Objectives:
- Know that structural isomers are compounds with the same molecular formula but different structural formulas.
- Be able to determine the possible structural formulas of an organic molecule, given its molecular formula.

Specification Reference 4.1.1

4. Structural Isomers

You can put the same atoms together in different ways to make completely different molecules. Two molecules are isomers if they have the same molecular formula but the atoms are arranged differently.

What are structural isomers?

In structural isomers, the molecular formula is the same, but the structural formula is different. There are three different types of structural isomer.

1. Chain isomers

The carbon skeleton can be arranged differently — for example, as a straight chain, or branched in different ways. Molecules that have different arrangements of the carbon skeleton are called **chain isomers**.

Examples — Maths Skills

There are different chain isomers of C_4H_{10}. The diagrams below show the straight chain isomer butane and a branched chain isomer methylpropane.

Here the longest carbon chain is 4 carbon atoms.
butane
Here the longest carbon chain is 3 carbon atoms.
methylpropane

Figure 1: Molecular models showing two chain isomers of C_4H_{10} — butane (left) and methylpropane (right).

There are different chain isomers of $C_4H_8O_2$. The diagrams below show the straight chain isomer butanoic acid and a branched chain isomer methylpropanoic acid.

Here the longest carbon chain is 4 carbon atoms.
butanoic acid
Here the longest carbon chain is 3 carbon atoms.
methylpropanoic acid

Exam Tip
You don't always have to draw all of the bonds when you're drawing a molecule — writing CH_3 next to a bond is just as good as drawing out the carbon atom, three bonds and three hydrogen atoms. But if you're asked for a displayed formula you must draw out all of the bonds to get the marks.

Chain isomers have similar chemical properties — but their physical properties, like boiling point, will be different because of the change in shape of the molecule.

2. Positional isomers

The skeleton and the functional group could be the same, only with the functional group attached to a different carbon atom. These are called **positional isomers**.

Example — Maths Skills

There are two positional isomers of C_4H_9Cl. The chlorine atom is attached to different carbon atoms in each isomer.

Tip: If the chlorine atom was attached to the carbon atom on the left, it would still be the same molecule — just drawn the other way round. It would still be 1-chlorobutane.

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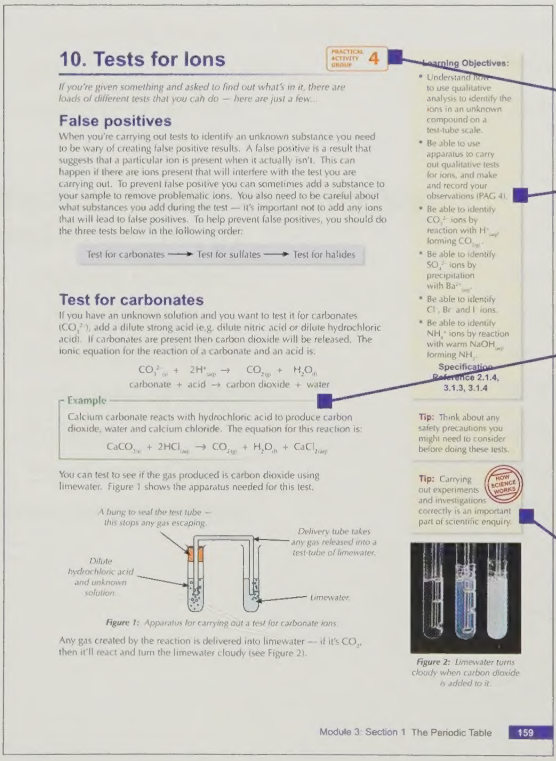

10. Tests for Ions

PRACTICAL ACTIVITY GROUP 4

If you're given something and asked to find out what's in it, there are loads of different tests that you can do — here are just a few...

False positives

When you're carrying out tests to identify an unknown substance you need to be wary of creating false positive results. A false positive is a result that suggests that a particular ion is present when it actually isn't. This can happen if there are ions present that will interfere with the test you are carrying out. To prevent false positive you can sometimes add a substance to your sample to remove problematic ions. You also need to be careful about what substances you add during the test — it's important not to add any ions that will lead to false positives. To help prevent false positives, you should do the three tests below in the following order:

Test for carbonates ⟶ Test for sulfates ⟶ Test for halides

Learning Objectives:
- Understand how to use qualitative analysis to identify the ions in an unknown compound on a test-tube scale.
- Be able to use apparatus to carry out qualitative tests for ions, and make and record your observations (PAG 4).
- Be able to identify CO_3^{2-} ions by reaction with $H^+_{(aq)}$ forming $CO_{2(g)}$.
- Be able to identify SO_4^{2-} ions by precipitation with $Ba^{2+}_{(aq)}$.
- Be able to identify Cl^-, Br^- and I^- ions.
- Be able to identify NH_4^+ ions by reaction with warm $NaOH_{(aq)}$ forming NH_3.

Specification Reference 2.1.4, 3.1.3, 3.1.4

Test for carbonates

If you have an unknown solution and you want to test it for carbonates (CO_3^{2-}), add a dilute strong acid (e.g. dilute nitric acid or dilute hydrochloric acid). If carbonates are present then carbon dioxide will be released. The ionic equation for the reaction of a carbonate and an acid is:

$$CO_{3\,(s)}^{2-} + 2H^+_{(aq)} \rightarrow CO_{2(g)} + H_2O_{(l)}$$
carbonate + acid → carbon dioxide + water

Example

Calcium carbonate reacts with hydrochloric acid to produce carbon dioxide, water and calcium chloride. The equation for this reaction is:

$$CaCO_{3(s)} + 2HCl_{(aq)} \rightarrow CO_{2(g)} + H_2O_{(l)} + CaCl_{2(aq)}$$

Tip: Think about any safety precautions you might need to consider before doing these tests.

You can test to see if the gas produced is carbon dioxide using limewater. Figure 1 shows the apparatus needed for this test.

A bung to seal the test tube — this stops any gas escaping.
Delivery tube takes any gas released into a test-tube of limewater.
Dilute hydrochloric acid and unknown solution.
Limewater.

Figure 1: Apparatus for carrying out a test for carbonate ions.

Tip: Carrying out experiments and investigations correctly is an important part of scientific enquiry.

Any gas created by the reaction is delivered into limewater — if it's CO_2, then it'll react and turn the limewater cloudy (see Figure 2).

Figure 2: Limewater turns cloudy when carbon dioxide is added to it.

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Practical Activity Groups

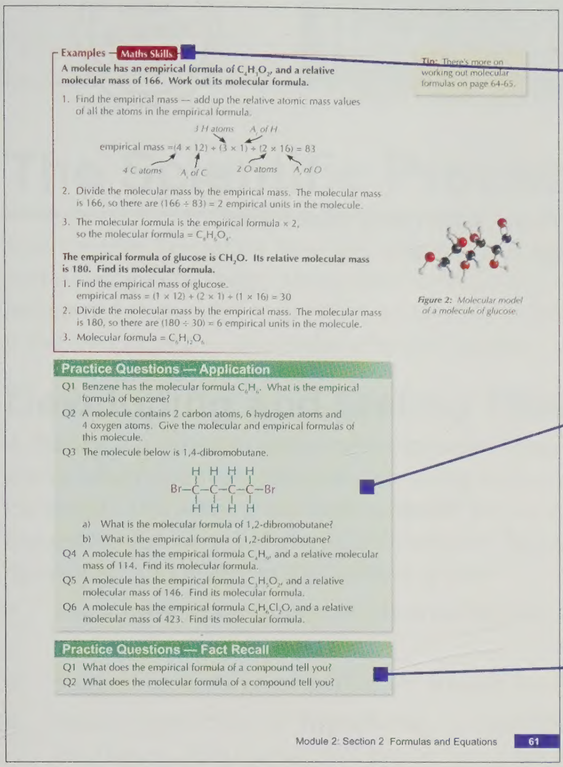
You need to show you've mastered some key practical skills in your Practical Endorsement. Information on the skills you need and opportunities to apply them are marked up throughout the book.

Examples

These are here to help you understand the theory.

How Science Works

- You need to know about How Science Works. There's a section on it at the front of the book.
- How Science Works is also covered throughout the book wherever you see this symbol.



Examples — **Maths Skills**

A molecule has an empirical formula of $C_4H_3O_2$, and a relative molecular mass of 166. Work out its molecular formula.

1. Find the empirical mass — add up the relative atomic mass values of all the atoms in the empirical formula.

   empirical mass = $(4 \times 12) + (3 \times 1) + (2 \times 16) = 83$

   4 C atoms, *A_r of C*, *3 H atoms*, *A_r of H*, *2 O atoms*, *A_r of O*
2. Divide the molecular mass by the empirical mass. The molecular mass is 166, so there are $(166 \div 83) = 2$ empirical units in the molecule.
3. The molecular formula is the empirical formula × 2, so the molecular formula = $C_8H_6O_4$.

The empirical formula of glucose is CH_2O. Its relative molecular mass is 180. Find its molecular formula.

1. Find the empirical mass of glucose.
   empirical mass = $(1 \times 12) + (2 \times 1) + (1 \times 16) = 30$
2. Divide the molecular mass by the empirical mass. The molecular mass is 180, so there are $(180 \div 30) = 6$ empirical units in the molecule.
3. Molecular formula = $C_6H_{12}O_6$

Tip: There's more on working out molecular formulas on page 64-65.

Figure 2: Molecular model of a molecule of glucose.

Practice Questions — Application

Q1 Benzene has the molecular formula C_6H_6. What is the empirical formula of benzene?

Q2 A molecule contains 2 carbon atoms, 6 hydrogen atoms and 4 oxygen atoms. Give the molecular and empirical formulas of this molecule.

Q3 The molecule below is 1,4-dibromobutane.

a) What is the molecular formula of 1,2-dibromobutane?

b) What is the empirical formula of 1,2-dibromobutane?

Q4 A molecule has the empirical formula C_4H_9, and a relative molecular mass of 114. Find its molecular formula.

Q5 A molecule has the empirical formula $C_3H_5O_2$, and a relative molecular mass of 146. Find its molecular formula.

Q6 A molecule has the empirical formula $C_4H_6Cl_2O$, and a relative molecular mass of 423. Find its molecular formula.

Practice Questions — Fact Recall

Q1 What does the empirical formula of a compound tell you?

Q2 What does the molecular formula of a compound tell you?

Module 2: Section 2 Formulas and Equations 61

Maths Skills

There's a range of maths skills you could be expected to apply in your exams. Examples that show these maths skills in action are marked up like this. There's also a maths skills section at the back of the book.

Practice Questions — Application

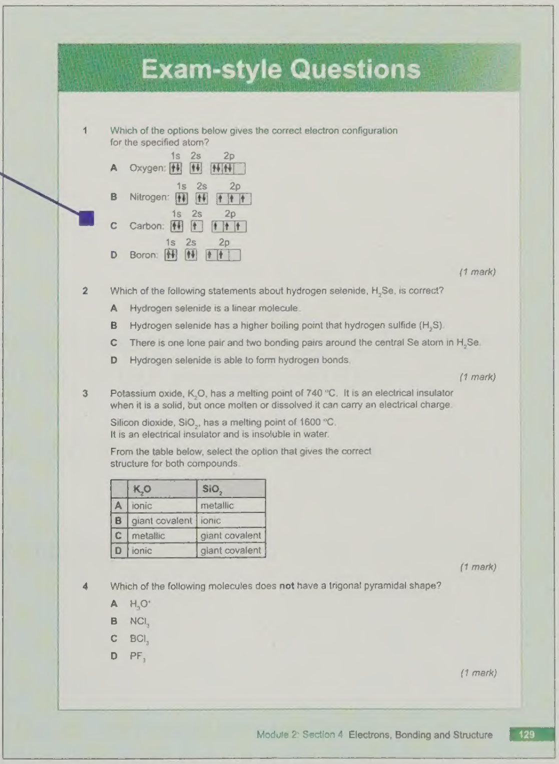
- Annoyingly, the examiners expect you to be able to apply your knowledge to new situations — these questions are here to give you plenty of practice at doing this.
- All the answers are in the back of the book (including any calculation workings).

Practice Questions — Fact Recall

- There are a lot of facts you need to learn — these questions are here to test that you know them.
- All the answers are in the back of the book.

Exam-style Questions

- Practising exam-style questions is really important — you'll find some at the end of each section.
- They're the same style as the ones you'll get in the real exams — some will test your knowledge and understanding and some will test that you can apply your knowledge.
- All the answers are in the back of the book, along with a mark scheme to show you how you get the marks.



Exam-style Questions

1 Which of the options below gives the correct electron configuration for the specified atom?

A Oxygen: 1s ⇅ 2s ⇅ 2p ⇅ ⇅ ☐

B Nitrogen: 1s ⇅ 2s ⇅ 2p ↑ ↑ ↑

C Carbon: 1s ⇅ 2s ↑ 2p ↑ ↑ ↑

D Boron: 1s ⇅ 2s ⇅ 2p ↑ ↑ ☐

(1 mark)

2 Which of the following statements about hydrogen selenide, H_2Se, is correct?

A Hydrogen selenide is a linear molecule.

B Hydrogen selenide has a higher boiling point that hydrogen sulfide (H_2S).

C There is one lone pair and two bonding pairs around the central Se atom in H_2Se.

D Hydrogen selenide is able to form hydrogen bonds.

(1 mark)

3 Potassium oxide, K_2O, has a melting point of 740 °C. It is an electrical insulator when it is a solid, but once molten or dissolved it can carry an electrical charge.

Silicon dioxide, SiO_2, has a melting point of 1600 °C.
It is an electrical insulator and is insoluble in water.

From the table below, select the option that gives the correct structure for both compounds.

	K_2O	SiO_2
A	ionic	metallic
B	giant covalent	ionic
C	metallic	giant covalent
D	ionic	giant covalent

(1 mark)

4 Which of the following molecules does **not** have a trigonal pyramidal shape?

A H_3O^+

B NCl_3

C BCl_3

D PF_3

(1 mark)

Module 2: Section 4 Electrons, Bonding and Structure 129

Exam Help

There's a section at the back of the book stuffed full of things to help with your exams.

Glossary

There's a glossary at the back of the book full of useful words — perfect for looking up key words and their meanings.

Published by CGP

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How Science Works

The Scientific Process

Science tries to explain how and why things happen. It's all about seeking and gaining knowledge about the world around us. Scientists do this by asking questions and suggesting answers and then testing them to see if they're correct — this is the scientific process.

Developing and testing theories

A **theory** is a possible explanation for something. Theories usually come about when scientists observe something and wonder why or how it happens. (Scientists also sometimes form a **model** too — a simplified picture or representation of a real physical situation.) Scientific theories and models are developed and tested in the following way:

- Ask a question — make an observation and ask why or how whatever you've observed happens.
- Suggest an answer, or part of an answer, by forming a theory or a model.
- Make a prediction or **hypothesis** — a specific testable statement, based on the theory, about what will happen in a test situation.
- Carry out tests — to provide evidence that will support the prediction or refute it.

Tip: A theory is only scientific if it can be tested.

Tip: The results of one test can't prove that a theory is true — they can only suggest that it's true. They can however disprove a theory — show that it's wrong.

Examples

Question: Why does bromine water react easily with cyclohexene but not with benzene?

Theory: Benzene has a ring of carbon atoms with delocalised electrons, so the negative charge is spread over the whole molecule. This makes it more stable than if it contained three double bonds, with a region of high electron density at each double bond.

Hypothesis: The enthalpy change for the hydrogenation of benzene (an exothermic reaction — see pages 437-438) will be less than three times the enthalpy change of the hydrogenation of cyclohexene, which contains one double bond.

Test: Use a calorimeter to measure the enthalpies of hydrogenation of benzene and cyclohexene. If the value for benzene is less than three times the value for cyclohexene, then the evidence supports the hypothesis.

Question: How do substances change during a redox reaction?

Theory: During a redox reaction electrons move from one substance to another.

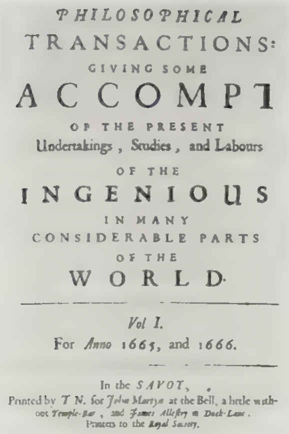
Hypothesis: When electrons move, a current flows. So a current will flow between the electrodes of an electrochemical cell when an oxidation reaction takes place at one electrode and a reduction reaction at the other.

Test: Set up an electrochemical cell using substances with different electrode potentials. Put an ammeter in the circuit and observe whether a current is flowing. If it is, then this evidence supports the hypothesis.

Tip: You couldn't carry out this test in your school or college lab — you'd need specialist equipment.

Tip: Hydrogenation of 1 mole of cyclohexene is the addition of 1 mole of hydrogen. Hydrogenation of 1 mole of benzene is the addition of 3 moles of hydrogen.

Tip: See pages 437-438 for more on the stability of benzene compared to alkenes.



PHILOSOPHICAL
TRANSACTIONS:
GIVING SOME
ACCOMPT
OF THE PRESENT
Undertakings, Studies, and Labours
OF THE
INGENIOUS
IN MANY
CONSIDERABLE PARTS
OF THE
WORLD.

Vol I.
For *Anno* 1665, and 1666.

In the *SAVOY*,
Printed by *T. N.* for *John Martyn* at the Bell, a little without *Temple-Bar*, and *James Allestry* in *Duck-Lane*.
Printers to the *Royal Society*.

Figure 1: *The first British scientific journal, 'Philosophical Transactions of the Royal Society', published in 1665.*

Communicating results

The results of testing a scientific theory are published — scientists need to let others know about their work. Scientists publish their results in scientific journals (see Figure 1). These are just like normal magazines, only they contain scientific reports (called papers) instead of the latest celebrity gossip.

Scientists use standard terminology when writing their reports. This way they know that other scientists will understand them. For instance, there are internationally agreed rules for naming organic compounds, so that scientists across the world will know exactly what substance is being referred to.

Scientific reports are similar to the lab write-ups you do in school. And just as a lab write-up is reviewed (marked) by your teacher, reports in scientific journals undergo **peer review** before they're published. The report is sent out to peers — other scientists who are experts in the same area. They go through it bit by bit, examining the methods and data, and checking it's all clear and logical. Thorough evaluation allows decisions to be made about what makes a good methodology or experimental technique. Individual scientists may have their own ethical codes (based on their personal moral or religious beliefs), but having their work scrutinised by other scientists helps to reduce the effect of personal bias on the conclusions drawn from the results.

When the report is approved, it's published. This makes sure that work published in scientific journals is of a good standard. But peer review can't guarantee the science is correct — other scientists still need to reproduce it. Sometimes mistakes are made and bad work is published. Peer review isn't perfect but it's probably the best way for scientists to self-regulate their work and to publish quality reports.

Tip: Scientific research is often funded by companies who have a vested interest in its outcomes. Scientists are ethically obliged to make sure that this does not bias their results.

Validating theories

Other scientists read the published theories and results, and try to test the theory themselves. This involves repeating the exact same experiments, using the theory to make new predictions, and then testing them with new experiments. This is known as **validation**. If all the experiments in the world provide evidence to back it up, the theory is thought of as scientific 'fact' (for now). If new evidence comes to light that conflicts with the current evidence, the theory is questioned all over again. More rounds of testing will be carried out to try to find out where the theory falls down. This is how the scientific process works — evidence supports a theory, loads of other scientists read it and test it for themselves, eventually all the scientists in the world agree with it and then bingo, you get to learn it.

Tip: Once an experimental method is found to give good evidence it becomes a protocol — an accepted method to test that particular thing that all scientists can use.

Example

The structure of benzene

Benzene is an organic molecule with the formula C_6H_6. It was first purified in 1825, but nobody knew back then what its structure was like.

In 1865, Kekulé suggested a possible structure for the benzene molecule. His idea was a ring of six carbon atoms with alternate double and single bonds between them, with one hydrogen atom bonded to each carbon.

But in the 20th century, data from X-ray diffraction studies and enthalpy experiments suggested that the Kekulé model was wrong. So scientists came up with a new model (the delocalised electron model — see Figure 2) that fitted the new data better. (There's lots more about this on pages 436 and 437). This is the model of the benzene molecule that we use today.

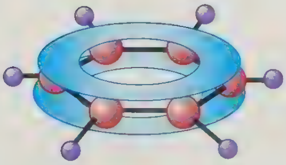


Figure 2: *A representation of the delocalised electron model of benzene.*

How do theories evolve?

Our currently accepted theories have survived this 'trial by evidence'. They've been tested over and over again and each time the results have backed them up. But they never become totally indisputable fact. Scientific breakthroughs or advances could provide new ways to question and test a theory, which may lead to changes and challenges to it. Then the testing starts all over again. This is the tentative nature of scientific knowledge. It's always changing and evolving.

Tip: Sometimes data from one experiment can be the starting point for developing a new theory.

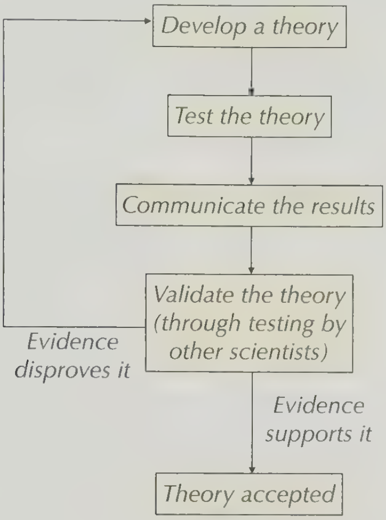


Figure 3: *Flow diagram summarising the scientific process.*

Example

CFCs and the ozone layer

When CFCs were first used in fridges in the 1930s, scientists thought they were problem-free — well, why not? There was no evidence to say otherwise. It was decades before anyone found out that CFCs were actually making a whopping great hole in the ozone layer.

A couple of scientists developed a theory that CFCs were destroying ozone in the stratosphere, and this was tested, shared and validated by other scientists worldwide. The rigour of the scientific process meant that there was strong enough evidence against CFCs that governments could impose bans and restrictions in order to protect the ozone layer.

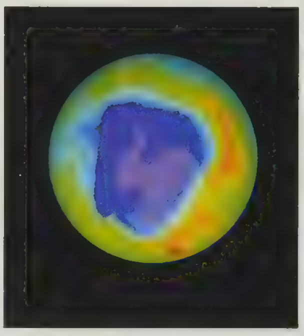


Figure 4: *The Antarctic ozone hole.*

Collecting evidence

1. Evidence from lab experiments

Results from controlled experiments in laboratories are great. A lab is the easiest place to control **variables** so that they're all kept constant (except for the one you're investigating). This means you can draw meaningful conclusions.

Example

Reaction yields

If you're investigating how the concentration of a reactant affects the yield of a reaction, you need to keep everything constant except for the concentration. This means controlling things like the temperature of the reaction mixture, the volumes used, etc. Otherwise you won't know if it's the change in concentration that's affecting the yield, or something else.

2. Investigations outside the lab

There are things you can't study in a lab. And outside the lab controlling the variables is tricky, if not impossible.

Example

How effective is cisplatin as an anti-cancer drug?

There are always differences between groups of people. The best you can do is to have a well-designed study using matched groups of people — choose two groups of patients (those who are being treated with cisplatin and those who aren't) which are as similar as possible (same type of cancer, same stage of cancer, same combinations of treatments, etc.). But you still can't rule out every possibility. There are always variables that can't be controlled so it's never a completely fair test. The size of the groups that you study is also important — the more people involved in the study the more reliable the results will be. And as with any study that's to do with people's health, there are ethical issues that have to be taken into consideration.

Science and decision-making

Lots of scientific work eventually leads to important discoveries that could benefit humankind and improve everyone's quality of life. But there are often risks attached (and almost always financial costs). Society (that's you, me and everyone else) must weigh up the information in order to make decisions — about the way we live, what we eat, what we drive, and so on. Information can also be used by politicians to devise policies and laws. However, there is not always enough information available for society and politicians to be certain about the decisions made. The scientific evidence we do have can also be overshadowed by other influences such as personal bias and beliefs, public opinion, and the media. Decisions are also affected by social, ethical and economic factors.

Tip: Don't get mixed up — it's not the scientists who make the decisions, it's society. Scientists just produce evidence to help society make the decisions.

Examples

Fuel cells

Hydrogen-oxygen fuel cells are an alternative to traditional fuel cells (see page 407). They're better for the environment than batteries, because their only waste product is water. But energy from another source is needed to produce the hydrogen and oxygen. And hydrogen is flammable, so it's tricky to store safely.

Developing drugs

Pharmaceutical drugs are expensive to develop and drug companies want to make money. So they put lots of effort into developing drugs that they can sell for a good price. Society has to consider the cost of buying drugs — the NHS can't afford the most expensive drugs without sacrificing other things.

Disposal of plastics

Synthetic polymers are very useful — they're cheap to produce and very durable. But they're hard to dispose of (they don't break down easily). So we need to make choices about how we can best dispose of plastics and whether we should try to reduce the amount that we use, or work to develop more biodegradable plastics.

Figure 5: *Waste plastic on a landfill site.*

Module 1 Development of Practical Skills

Practical Skills in Chemistry

HOW SCIENCE WORKS

Practicals and experiments crop up in every area of Chemistry and they can't be studied in isolation from the rest of your course. So this module draws on Chemistry knowledge that you'll learn in later modules. You should use it as a resource to help you apply the things you'll learn throughout the course in order to solve problems in a practical context.

1. Planning Experiments

You'll get to do loads of practicals in class during this course, which is great. Unfortunately, you can also get tested on how to carry out experiments in your exam. The first thing you need is a good plan...

Learning Objectives:

- Know how to design experiments, including to solve problems set in a practical context.
- Be able to identify variables that must be controlled, where appropriate.
- Be able to evaluate whether an experimental method is appropriate to meet the expected outcomes.

Specification Reference 1.1.1

Initial planning

It's really important to plan an experiment well if you want to get accurate and precise results. Before you even touch a piece of glassware, there are a few things you need to think about.

First, you have to identify what it is that you're trying to work out. This is the aim of your experiment. It could be something like 'how does the rate of this reaction change at different temperatures', or 'what is the concentration of this solution'. Once you know your aim, you can identify the independent, dependent and other **variables** (see below for more on variables). You can then decide what data you need to collect and how to collect it. This includes working out what equipment you'll need to use — it needs to be the right size and sensitivity so that your results are accurate.

Before you get going, there are two more things to do. The first is to make a risk assessment and plan any safety precautions. This ensures that you minimise the risk from any hazards there might be in your experiment, such as harmful chemicals. You should then write your whole plan down in a detailed method.

Tip: Accurate results are close to the true answer. See page 21 for more on accurate and precise results.

Variables

You probably know this all off by heart but it's easy to get mixed up sometimes. So here's a quick recap. A variable is a quantity that has the potential to change, e.g. mass. There are two types of variable commonly referred to in experiments:

Independent variable — the thing that you change in an experiment.

Dependent variable — the thing that you measure in an experiment.

As well as the independent and dependent variables, you need to think of all the other variables in your experiment and plan ways to keep each of those the same. This is to make sure that your test is fair, and any changes in your dependent variable are only due to changes in the independent variable.

Example

You could investigate the effect of temperature on rate of reaction using the apparatus in Figure 1 below:

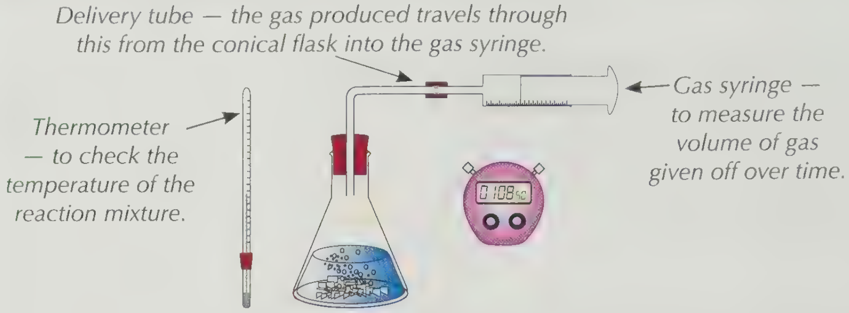

Delivery tube — the gas produced travels through this from the conical flask into the gas syringe.
Gas syringe — to measure the volume of gas given off over time.
Thermometer — to check the temperature of the reaction mixture.
0 108

Figure 1: Apparatus for measuring the rate of a reaction.

Tip: Any variables that aren't your independent or dependent variables, must be controlled so that they're always the same.

- The independent variable will be temperature.
- The dependent variable will be the amount of gas produced.
- All the other variables must be kept the same. These include the concentration and volume of solutions, mass of solid, pressure, the presence of a catalyst and the surface area of any solid reactants.

Types of data

Experiments often involve some sort of measurement to provide data. There are different types of data — and you need to know what they are.

1. Discrete data

You get discrete data by counting. E.g. the number of bubbles produced in a reaction would be discrete. You can't have 1.25 bubbles. That'd be daft.

Tip: To know the exact value of a piece of continuous data you'd need to have equipment that measured to an infinite number of decimal places — and they just don't exist.

2. Continuous data

A continuous variable can have any value on a scale. For example, the volume of gas produced or the mass of products from a reaction. You can never measure the exact value of a continuous variable.

3. Categoric data

A categoric variable has values that can be sorted into categories. For example, the colours of solutions might be blue, red and yellow (see Figure 2). Or types of material might be wood, steel and glass.

Figure 2: Different coloured solutions. Colour is a type of categoric data.

4. Ordered (ordinal) data

Ordered data is similar to categoric, but the categories can be put in order. For example, if you classify reactions as 'slow', 'fairly fast' and 'very fast' you'd have ordered data.

Choosing the right data to collect

HOW SCIENCE WORKS

The data you choose to collect should be something that changes and can be easily measured or observed over the course of your experiment.

Tip: You don't just need to think about what you're measuring in an experiment, but also how you'd measure it.

Example

You might want to measure the rate of the following reaction:

$$NaOH_{(aq)} + CH_3CH_2Br_{(l)} \rightarrow CH_3CH_2OH_{(l)} + NaBr_{(aq)}$$

There wouldn't be any point in collecting data about how the conductivity changes over the course of the reaction, for example, because there are salts in both the reactants and the products. But you could use a pH meter to measure how the pH changes from basic (due to sodium hydroxide) to almost neutral.

The data you collect also has to provide evidence that addresses the aim of your experiment and gives the right level of detail — there's no point collecting data that doesn't help answer your question.

Example

You might want to measure the enthalpy change of a reaction. It's no good just feeling whether the reaction vessel heats up or cools down — this tells you whether the reaction uses energy or gives out energy, but not what the enthalpy change actually is.

You also need to be careful about how often and how long you measure the temperature for. If you just measure the change over the first 30 seconds of the reaction then you'll only get the enthalpy change over that period of time, which isn't necessarily the total change. Instead, you should keep measuring the temperature until it stops changing. At this point, all the reactants should have been used up, and the reaction is complete. You can then work out the total change in temperature, and so the total enthalpy change.

Tip: The enthalpy change of a reaction is just the amount of energy taken in or given out by the reactants when they react to form the products. There's a whole section about enthalpy changes on pages 166-178.

Selecting equipment

HOW SCIENCE WORKS

Selecting the right apparatus may sound easy but it's something you need to think carefully about. Your equipment has to be appropriate for the specific experiment. It should be the right size and scale for whatever you're measuring, and it should have the right level of sensitivity to keep any errors in your measurement to a minimum.

Tip: You can find out how to calculate errors in your measurements on pages 21 and 22.

Example

In an experiment where you're measuring the volume of gas produced, you should think about the following things when choosing your equipment:

- The apparatus you use has to collect the gas, without letting any escape. For example, a gas syringe connected to a sealed vessel where the reaction is taking place (see Figure 3).
- The gas syringe needs to be big enough to collect all the gas produced during the experiment, or the plunger will just fall out the end. You might need to do some calculations to estimate how much gas will be produced, to work out what size of syringe to use.
- The gas syringe needs to measure to the right level of sensitivity. If you predict that about 10 cm^3 will be produced, it will be more accurate to use a syringe that is graduated to the nearest 0.5 cm^3 than to the nearest 1 cm^3.

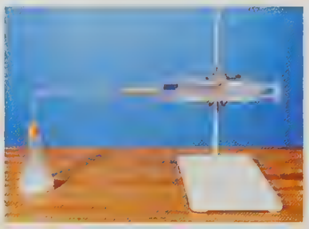


Figure 3: *Apparatus used to measure the volume of gas produced in a reaction.*

Drawing equipment

When you're writing out a method for your experiment, it's always a good idea to draw a labelled diagram showing how your apparatus will be set up. The easiest way to do this is to use a scientific drawing, where each piece of apparatus is drawn as if you're looking at its cross-section. Some basic pieces of equipment that you're likely to need to draw are shown in Figure 4.

Tip: There's more information about writing methods for experiments on page 8.

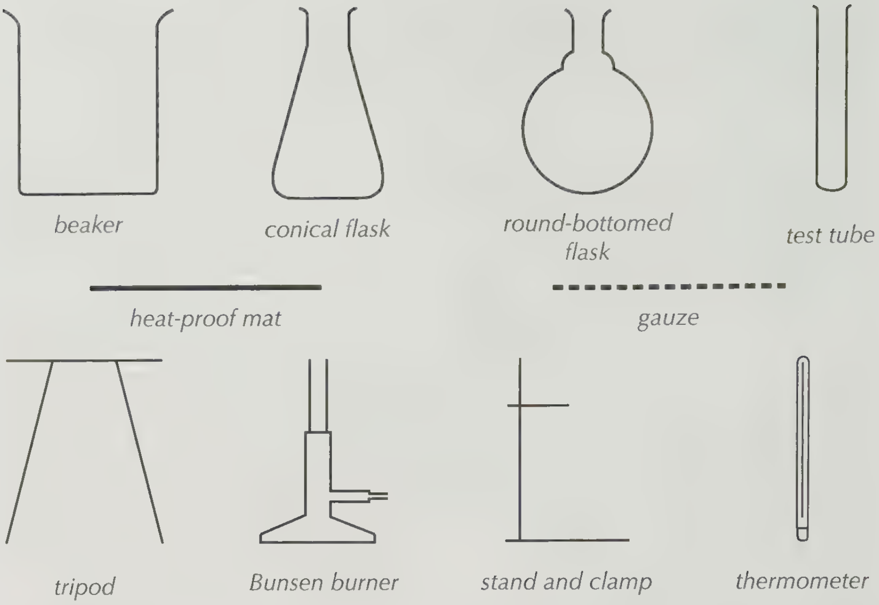


Figure 4: *Scientific diagrams of some basic laboratory equipment.*

Risk assessments

In order to work safely, you need to carry out a risk assessment for your experiment. To do this, you need to identify:

- All the dangers in the experiment, for example any hazardous compounds or naked flames.
- Who is at risk from these dangers — this could be you and your lab partner, but it could also be anyone who is in the same room or building.
- What can be done to reduce the risk. You should wear a lab coat and goggles as a standard precaution, but you may need to take other safety precautions, such as carrying out your experiment in a fume-hood, only using low concentrations or dilute solutions of reactive substances and preventing anything that can react with oxygen or water from coming into contact with them.

Writing a method

When writing a method, you need to make sure it's clear and detailed enough for anyone to follow — it's important that other people can recreate your experiment and get the same results. Make sure your method includes:

1. All substances and quantities to be used. You need to include the concentrations of any solutions, any catalysts that are needed and the conditions (such as temperature and pressure) that the experiment will be carried out at.
2. What variables you need to control and how to control them.
3. The exact apparatus needed, including sizes. A labelled diagram is usually helpful to show the set-up.
4. What data to collect and step-by-step instructions on how to collect it.
5. How to minimise any errors at each step. For example, how to reduce transfer errors (see pages 11 and 12).
6. Any safety precautions that should be taken.

Tip: None of the pieces of glassware are drawn with tops. This means that they're not sealed. If you want to draw a closed system, remember to draw a bung in the top.

Exam Tip
Always make sure the set-up is drawn correctly in your diagrams. This might mean making sure your diagram shows a closed system if you're collecting a gas, making sure any thermometers are positioned at the right point for where you're measuring the temperatures, or making sure that any equipment with a water flow shows it going in the right direction.

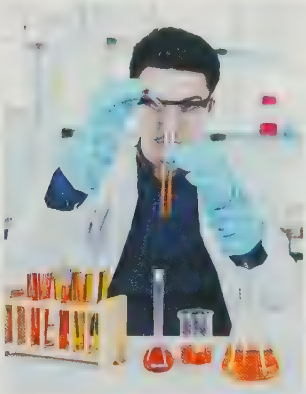


Figure 5: *A student wearing gloves, goggles and a lab coat to protect his skin, eyes and clothes from any hazardous substances.*

Exam Tip
It's easy to forget really simple instructions like making sure your solutions are mixed properly — make sure you include every step in your method or you may end up losing easy marks in the exam.

Example

Copper(II) sulfate is an ionic compound with the formula $CuSO_4$. Sometimes, water molecules can be incorporated into the ionic lattice. When this happens, the crystal is hydrated and has the formula $CuSO_4.xH_2O$. You can carry out an experiment with the aim of finding the value of x. To do this, you need to find the difference in mass between a sample of copper(II) sulfate when it is hydrated and anhydrous. Here's a method for the experiment:

PRACTICAL ACTIVITY GROUP 1

Tip: There's loads more about hydrated salts and calculating their molecular formulas on pages 81-82.

Tip: If something's anhydrous then it's got no water in it.

Equipment and substances:

- A mass balance
- A 30 cm^3 crucible
- A spatula
- A Bunsen burner on a heat-proof mat
- A tripod and gauze
- About 2 g hydrated copper(II) sulfate

Safety Precautions:

This experiment uses a naked flame, so care should be taken when nearby. The Bunsen burner should be placed on a heat-proof mat, and shouldn't be near any flammable substances. Care should be taken when heating the copper sulfate as, if it is overheated, toxic gas can be given off. If the sample begins to go black, you should stop heating it immediately. Allow all your apparatus to cool before touching it. Copper sulfate is harmful if swallowed and can irritate skin and eyes, so a lab coat, gloves and goggles should be worn.

Tip: You should be able to explain why each step in a method is necessary.

Method:

1. Zero the mass balance, and then use it to weigh the empty crucible. Record the mass of the empty crucible.
2. Weigh out approximately 2 g of hydrated copper sulfate into the crucible and record their combined mass.
3. Gently heat the crucible containing the hydrated copper sulfate using the set-up in Figure 6.

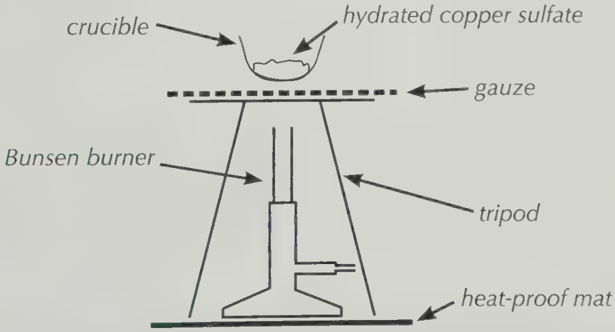


***Figure 6:** The set-up for an experiment to find the formula of hydrated copper sulfate.*

4. Heating the hydrated copper sulfate causes the water in the crystals to evaporate, leaving anhydrous copper sulfate in the crucible. Once all the copper sulfate has changed from blue to white, turn off the Bunsen burner and leave the crucible to cool.
5. When the crucible is cool, reweigh it and record the combined weight of the crucible and the anhydrous copper sulfate.

***Figure 7:** An experiment to find the formula of hydrated copper(II) sulfate.*

Tip: Once you've calculated the difference in mass between the hydrated and anhydrous sample you need to do some more calculations to find the value of x in the formula. You can find out how to do this on pages 81-82.

Once you've got your three recorded masses, you can then work out:

- The original mass of hydrated copper sulfate, which you calculate by subtracting the mass of the empty crucible from the combined mass of the crucible and the hydrated copper sulfate.
- The final mass of anhydrous copper sulfate, which you calculate by subtracting the mass of the empty crucible from the combined mass of the crucible and the anhydrous copper sulfate.
- The difference in mass between the sample when it is hydrated and anhydrous, by subtracting the final mass from the initial mass.

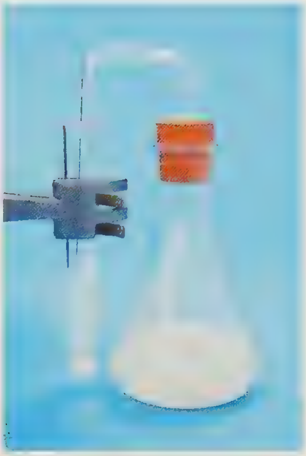


Figure 8: *The apparatus used to determine whether the gas given off by a reaction is carbon dioxide.*

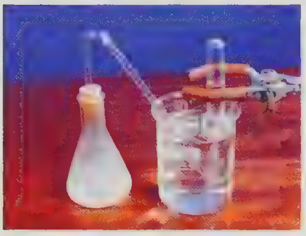


Figure 9: *Apparatus for collecting the gas given off in a reaction.*

Practice Questions — Application

Q1 A student wants to find out whether the gas given off when hydrochloric acid reacts with calcium carbonate is carbon dioxide. She does this by setting up a reaction between the two compounds in a sealed conical flask and bubbling the gas that is produced through a solution of limewater in a test tube. If the gas is carbon dioxide, then the solution of limewater should turn cloudy. The apparatus she uses is shown in Figure 8.

a) Draw a labelled scientific diagram of the apparatus used in this experiment.

b) Describe two hazards that might be associated with this experiment, and what you could do to reduce the risk.

Q2 A student wishes to determine the volume of gas given off in the first minute of an experiment. He suggests collecting the gas using test tubes inverted in a water bath (see Figure 9).
Explain why this is not an appropriate method of measuring how much gas has been given off, and suggest a better piece of equipment for carrying out this experiment.

Q3 Chloroalkanes and bromoalkanes react with water in the presence of silver nitrate and ethanol to form insoluble silver halide precipitates. The time taken for the precipitate to form depends on the rate of the reaction. A student wants to find out whether the rate of the reaction is affected by whether the haloalkane is a chloroalkane or a bromoalkane.

a) Identify the independent variable in this experiment.

b) What data could you collect to address the aim of the experiment?

c) Suggest two other variables in this experiment that would need to be kept constant.

Tip: A haloalkane is an organic molecule that contains carbon atoms, hydrogen atoms and halogen (fluorine, chlorine, bromine or iodine) atoms (see page 253).

Practice Questions — Fact Recall

Q1 What is an independent variable?

Q2 Is the colour of a solution categoric or continuous data?

Q3 Give three things you should consider when carrying out a risk assessment.

2. Practical Techniques

The way you carry out your experiment is important. You'll meet lots of specific techniques throughout this course, but there are some things you'll be doing all the time. You've probably met some of them before.

Learning Objectives:

- Know how to use a wide range of practical apparatus and techniques correctly.
- Be able to measure the mass of a solid (PAG 1).
- Be able to measure the volume of a liquid (PAG 2).
- Be able to measure the volume of a gas (PAG 1).
- Be able to measure temperature (PAG 3).
- Be able to make and record qualitative observations (PAG 4).
- Be able to use reflux in the synthesis of an organic liquid (PAG 5).
- Be able to use distillation in the synthesis of an organic liquid (PAG 5).
- Be able to use a separating funnel to purify an organic liquid (PAG 5).

Specification Reference 1.1.2

Precise results

The results of any experiment you carry out should be **precise**. This means that they are **repeatable** and **reproducible**. Repeatable means that if the same person does the experiment again using the same methods and equipment, they'll get the same results. Reproducible means that if someone else does the experiment, or a different method or piece of equipment is used, the results will still be the same.

To make sure your results are precise, you need to minimise any errors that might sneak into your data. This includes using apparatus and techniques correctly, taking measurements correctly and repeating your experiments and calculating a mean.

Measuring the mass of solids

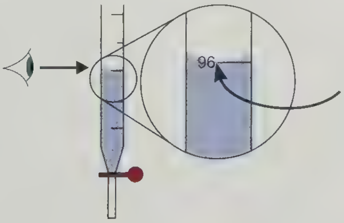
PRACTICAL ACTIVITY GROUP 1

You weigh solids using a balance. To do this you should put the container you are weighing your substance into on the balance, and make sure the balance is set to exactly zero before you start weighing out your substance. Once you've measured a quantity of a substance you need to be careful you don't lose any. In particular, think about how to minimise losses as you transfer the solid from the measuring equipment into another container. For example, if you're making up a standard solution, you could wash any remaining solid into the new container using the solvent. Or you could reweigh the weighing container after you've transferred the solid so you can work out exactly how much you added to your experiment.

Measuring the volumes of liquids

PRACTICAL ACTIVITY GROUP 2

There are a few methods you might use to measure the volume of a liquid. Whichever method you use, always read the volume from the bottom of the meniscus (the curved upper surface of the liquid) when it's at eye level (see Figure 1).



Read volumes from here — the bottom of the meniscus.

Figure 1: *The technique for correctly measuring the volume of a liquid.*

Pipettes

Pipettes are long, narrow tubes that are used to suck up an accurate volume of liquid and transfer it to another container. They are often calibrated to allow for the fact that the last drop of liquid stays in the pipette when the liquid is ejected. This reduces transfer errors.

Figure 2: *A scientist using a pipette to measure out an accurate volume of liquid.*

Burettes

Burettes measure from top to bottom (so when they are full, the scale reads zero). They have a tap at the bottom which you can use to release the liquid into another container (you can even release it drop by drop). To use a burette, take an initial reading, and once you've released as much liquid as you want, take a final reading. The difference between the readings tells you how much liquid you used.

Figure 3: *A student using a burette.*

Volumetric flasks

Volumetric flasks allow you to accurately measure a very specific volume of liquid. They come in various sizes (e.g. 100 ml, 250 ml) and there's a line on the neck that marks the volume that they measure. They're used to make accurate dilutions and standard solutions (solutions with a precisely known concentration). To use them, first measure out the liquid or solid that's being diluted or dissolved into a separate measuring vessel. Add this substance to the volumetric flask and rinse out the measuring vessel into the volumetric flask with some solvent to make sure everything's been transferred. Then fill the flask with solvent to the bottom of the neck. Fill the neck drop by drop until the bottom of the meniscus is level with the line. Stopper the flask and invert it a couple of times to make sure that the solution is properly mixed.

Figure 4: *Using a volumetric flask to prepare a solution.*

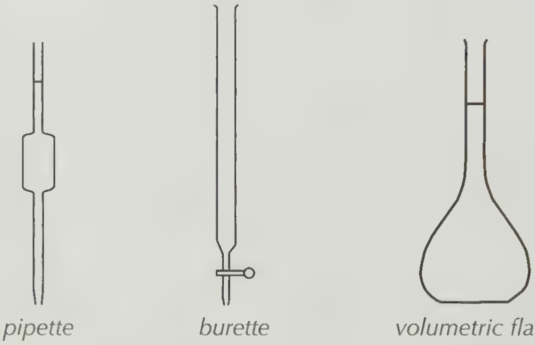


Figure 5: *Scientific diagrams of some equipment used to measure liquids.*

Tip: Burettes and volumetric flasks are both used in titration experiments — see page 83 for more about titrations. Gas syringes can be used to follow the rate of a reaction (see pages 185-187), and in moles determination experiments (see page 54).

Measuring the volumes of gases

PRACTICAL ACTIVITY GROUP 1

Gases can be measured with a gas syringe. They should be measured at room temperature and pressure as the volume of a gas changes with temperature and pressure. Before you use the syringe, you should make sure it's completely sealed and that the plunger moves smoothly.

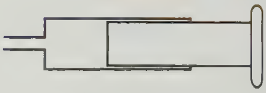


Figure 6: *A scientific diagram of a gas syringe.*

Measuring temperature

PRACTICAL ACTIVITY GROUP 3

You can use a thermometer or a temperature probe to measure the temperature of a substance (a temperature probe is like a thermometer but it will always have a digital display). Think about where you need to take your measurement from — if you're measuring the temperature of a liquid, the bulb of the thermometer or probe should be submerged in the substance you're measuring. If you're measuring the temperature of a gas as it's distilled from a liquid, then the bulb of your thermometer or temperature probe should be at the outlet of the distillation apparatus. This is so you know the temperature being measured is the same as the temperature of the substance that is being distilled. Always wait for the temperature to stabilise before taking an initial reading and if you're using a thermometer with a scale, read off your measurement at eye level to make sure it's accurate.

Tip: Measuring temperature accurately is really important in enthalpy determination. See page 171 for more on experiments to determine enthalpy changes.

Making qualitative observations

Qualitative tests measure physical qualities (e.g. colour) while **quantitative** tests measure numerical data, (e.g. mass). Qualitative tests can be harder to reproduce because they're often subjective (based on opinion), such as describing the colour or cloudiness of a solution.

Example

In an experiment to test whether a reaction is exothermic (gives out heat) or endothermic (takes in heat), one person might say that the reaction vessel 'warms up slightly', whilst someone else might say that the same vessel gets 'very hot'. These are qualitative observations and it's hard to make them reproducible because the observation is based on the opinion of the person carrying out the experiment.

If a thermometer was used to measure the change in temperature over the reaction, then the reading on the thermometer would be the same no matter who took the measurement. This is a quantitative observation.

Tip: See pages 159-161 for examples of qualitative tests for ions.

There are ways to reduce the subjectivity of qualitative observations. E.g.:

- If you're looking for a colour change, put a white background behind your reaction container.
- If you're looking for a precipitate to form, mark an X on a piece of paper and place it under the reaction container. Your solution is 'cloudy' when you can no longer see the X (see Figure 7).

PRACTICAL ACTIVITY GROUP 4

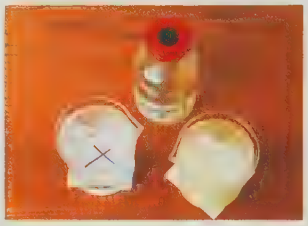


Figure 7: An experiment to time how long it takes for a solution to go cloudy.

Organic techniques

PRACTICAL ACTIVITY GROUP 5

Synthesis is used to make one organic compound from another. There are a number of techniques that chemists use to make and purify products:

Tip: Always carry out a full risk assessment before using any of the organic techniques on these pages.

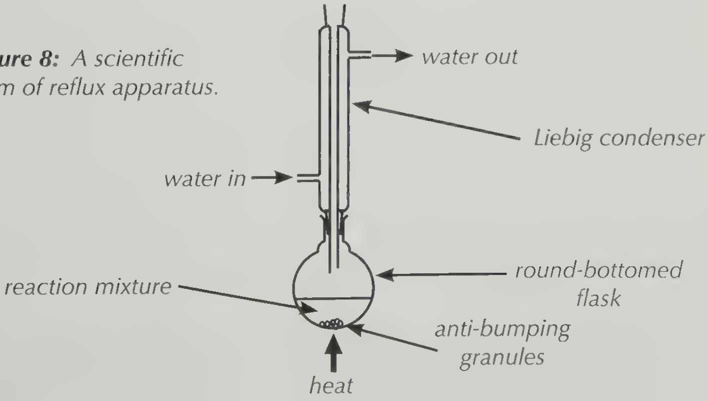
Reflux

Reflux is used when making a volatile organic product (one that evaporates easily) from compounds that need to be heated in order to react. The reaction mixture is heated in a flask fitted with a condenser so that any materials that evaporate will condense and drip back into the mixture. This stops you losing any of the reactants or products from the mixture during the reaction.

Tip: There's more about using reflux to synthesise organic compounds on page 279.

Tip: Organic compounds are just molecules that contain carbon.

Figure 8: A scientific diagram of reflux apparatus.



Tip: Organic compounds are often flammable, so it's best to heat them with a hot plate or a water bath instead of a Bunsen burner.

Tip: Anti-bumping granules help the mixture to boil evenly, and stop it suddenly bubbling up.

Distillation

Distillation involves gently heating a mixture so that the compounds evaporate off in order of increasing boiling point. This allows the different compounds to be collected separately as they will evaporate out of the mixture at different temperatures. Distillation can be done during a reaction to collect a product as it forms, or after the reaction is finished to purify the mixture.

Tip: There's more about using distillation to synthesise and purify organic compounds on pages 279-280.

Tip: If you need to draw a distillation diagram, make sure that the bulb of the thermometer is level with the outlet.

Tip: The flow of water in a condenser always goes in at the bottom and out at the top, stopping any air getting trapped which would heat up and disrupt how the water cools the condenser.

Tip: There's more about using separation to purify an organic liquid on pages 280-281.

Tip: Organic liquids are normally less dense than water so the organic layer will be the top layer in the separating funnel.

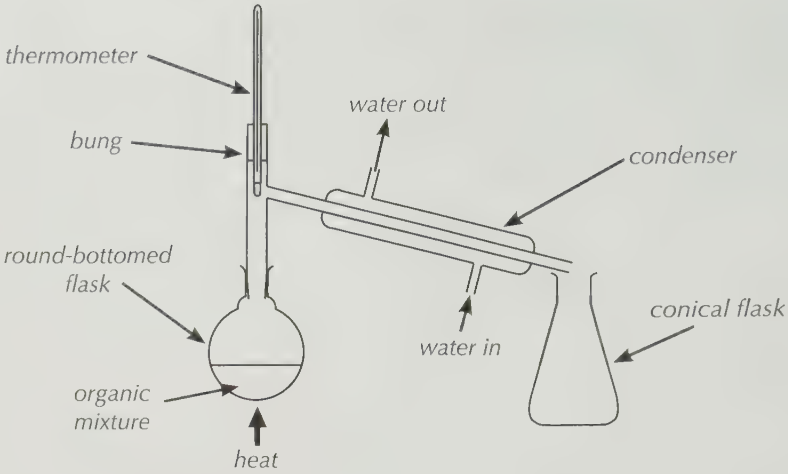


Figure 9: *A scientific diagram of distillation apparatus.*

Removing water soluble impurities

You can use a separating apparatus to purify organic substances from any impurities that are soluble in water. You add water to an organic mixture in a separating funnel, any water soluble impurities move out of the organic layer and dissolve in the aqueous layer. The layers have different densities so are easy to separate.

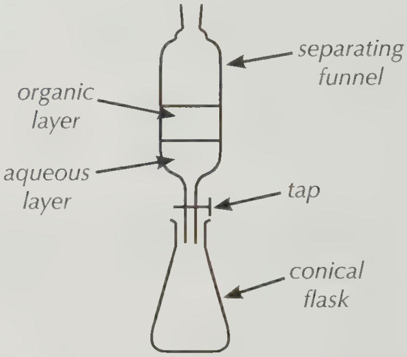


Figure 10: *A scientific diagram of separating apparatus.*

Practice Questions — Application

Q1 Two students carry out an experiment to see how long it takes a reaction mixture to turn cloudy. Despite carrying out identical experiments, there is a difference of 30 seconds between their results. Suggest what they could do to improve the agreement of their results.

Q2 A student is making up a standard solution.

a) Suggest what piece of apparatus the student should use to make up his solution in.

b) How could the student minimise transfer errors when moving the solid from the weighing vessel into the apparatus in part a)?

Practice Questions — Fact Recall

Q1 Suggest how you could reduce transfer errors when transferring a solid from a weighing vessel into a container containing a solution of known volume and concentration.

Q2 Name three pieces of apparatus you could use to measure the volume of a liquid.

Q3 Describe the process of distillation.

3. Tables and Data

When you're carrying out experiments, you usually need to collect your data in a table — it makes it easier to analyse. You'll then need to check your data's consistent and do a bit of maths before you get your final results.

Learning Objectives:

- Know how to present observations and data in an appropriate format.
- Be able to identify anomalies in experimental measurements.
- Be able to use appropriate mathematical skills for analysis of quantitative data.
- Know how to use significant figures appropriately and use appropriate units for measurement.
- Know how to process qualitative and quantitative experimental results.

Specification Reference
1.1.2, 1.1.3, 1.1.4

Tables of data

Before you start your experiment, make a table to write your results in. When you draw a table, make sure you include enough rows and columns to record all of the data you need. You might also need to include a column for processing your data (e.g. working out an average). Make sure each column and row has a heading so you know what's going to be recorded where. It's usually a good idea to include the units of your measurements in the column heading, not the table itself.

You'll need to repeat each test at least three times. If your results are consistent it's a good indication that they're precise. Figure 1 (below) is the sort of table you might use when you investigate the effect of temperature on reaction rate. (You'd then have to add rows for different temperatures.)

Temperature (°C)	Time (s)	Volume of gas evolved (cm^3)			Average volume of gas evolved (cm^3)
		Run 1	Run 2	Run 3	
20.0	10	8.1	7.6	8.5	
	20	17.7	19.0	20.1	
	30	28.5	20.1	30.0	

Figure 1: *Table of results showing the effect of temperature on the rate of reaction.*

Anomalous results

Watch out for **anomalous results**. These are ones that don't fit in with the other values and are likely to be wrong. They're usually due to random errors, such as making a mistake when measuring. You should ignore anomalous results when you calculate averages or draw lines of best fit.

Example

Look at Figure 1 again — the volume of gas evolved after 30 s in Run 2 looks like it might be an anomalous result. It's much lower than the values in the other two runs. One reason it could be lower is that the syringe plunger could have got stuck during the experiment.

Tip: Scientists need to be able to present and communicate their results clearly so that other people can understand what they've discovered.

HOW SCIENCE WORKS

Tip: A fancy way of saying a result is anomalous is to say that it 'isn't concordant' with the other results.

Calculating means

A mean is just an **average** of your repeated results. It's normally more **precise** than an individual result because it helps to balance out any random errors in your data (see page 22). To calculate the mean result, first remove any anomalous results. Then add up all the other measurements from each repeat and divide by the number of (non-anomalous) measurements.

Example — **Maths Skills**

The average volume of gas evolved at each time point in Figure 1 is:

After 10 seconds: $(8.1 + 7.6 + 8.5) \div 3 = 8.1\ cm^3$

After 20 seconds: $(17.7 + 19.0 + 20.1 \div 3) = 18.9\ cm^3$

After 30 seconds: The result at 30 seconds in Run 2 is anomalously low, so ignore it when calculating the mean. $(28.5 + 30.0) \div 2 = 29.3\ cm^3$.

Units and significant figures

Units are really important — 10 g is a bit different from 10 kg, so don't forget to add them to your tables and graphs. It's often a good idea to write down the units on each line of any calculations you do — it makes things less confusing, particularly if you need to convert between two different units.

Tip: There are loads of useful unit conversions on pages 548-549.

It's also important to keep track of significant figures when working with data. The first significant figure is the first number of a measurement that isn't zero. The second, third and fourth significant figures (and so on) are the numbers that come directly after the first significant figure, whether or not they are zero. The general rule is that the answer to any calculation should be rounded to the lowest number of significant figures (s.f.) given in the question. If there are lots of steps in your calculation before you reach the final answer, you don't need to round your intermediate answers. Rounding too early could make your final answer less accurate.

Exam Tip
Always write down the number of significant figures you've rounded to after your answer — it shows you really know what you're talking about.

Example — **Maths Skills**

Given that the experiment in Figure 1 was carried out at a pressure of 1.0×10^5 Pa, calculate how many moles of gas were evolved after 20 seconds using the ideal gas equation, $pV = nRT$.
(At 20 °C, an average of 18.9 cm^3 of gas was evolved after 20 seconds.)

- First you have to convert all the values into standard units:

  To convert from °C to K, add 273: $20.0 + 273 = 293$ K

  To convert from cm^3 to m^3, divide by 1 000 000:

  $$18.9 \div 1\,000\,000 = 1.89 \times 10^{-5}\ m^3$$

- Rearrange the equation to make n (the number of moles) the subject:

  $$n = (pV) \div (RT)$$

  $$n = ((1.0 \times 10^5\ Pa) \times (1.89 \times 10^{-5}\ m^3)) \div (8.31\ J\ K^{-1}\ mol^{-1} \times 293\ K)$$
  $$= 7.7623489... \times 10^{-4}\ mol$$

- From the original values, temperature and volume were both given to three significant figures, and pressure was given to two significant figures. So the final answer should be rounded to two significant figures: $n = 7.8 \times 10^{-4}$ mol (2 s.f.)

Tip: When using the ideal gas equation, temperature should be in K, pressure should be in Pa and volume should be in m^3. There's more about the ideal gas equation on page 52.

Tip: R, the gas constant, is 8.31 J K^{-1} mol^{-1}.

Practice Questions — Application

Q1 The table below shows an extract from the results of an experiment investigating the rates at which different substances increase in temperature when heated in the same way. Calculate the mean for each of the data points when the experiment is carried out for water.

Substance	Time (s)	Temperature (°C)		
		Repeat 1	Repeat 2	Repeat 3
Water	0	18.7	18.4	19.0
	20	22.0	21.7	21.8
	40	24.6	25.0	24.8

Q2 An experiment to measure the change in mass when 1.0 g of hydrated zinc chloride is heated until it is anhydrous (has lost all its water) is repeated three times. The change in mass of the sample for each repeat is: 0.36 g, 0.35 g, 0.33 g. Given that the molar mass of water is 18.0, calculate the average number of moles of water lost from the sample in the experiment.

Tip: The formula moles = mass ÷ molar mass will be useful in Question 2.

4. Graphs and Charts

Once you've identified any anomalous results, and calculated your mean results, the next step is normally to put all your data into a graph.

Types of graphs and charts

You'll usually be expected to make a graph of your results. Graphs make your data easier to understand — so long as you choose the right type.

Bar charts

You should use a bar chart when one of your data sets is categoric or ordered data, like in Figure 1.

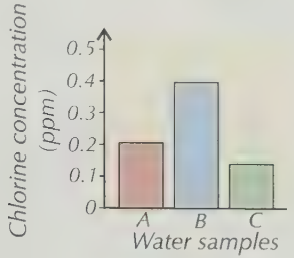


Figure 1: *Bar chart to show chlorine concentration in water samples.*

Pie charts

Pie charts are normally used to display categoric data, like in Figure 2.

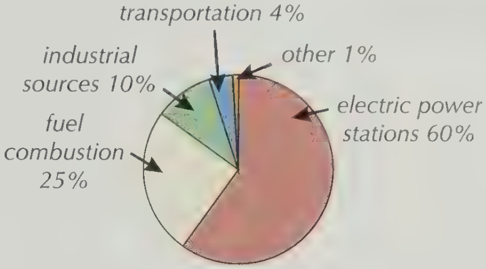


Figure 2: *Pie chart to show sources of a country's sulfur dioxide emissions.*

Scatter graphs

Scatter graphs, like Figures 3 and 4, are great for showing how two sets of continuous data are related (or correlated — see below). Don't try to join all the points — draw a line of best fit to show the trend.

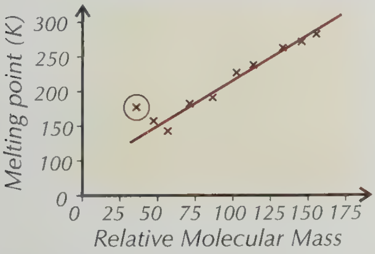


Figure 3: *Scatter graph showing the relationship between M_r and melting point of some alcohols.*

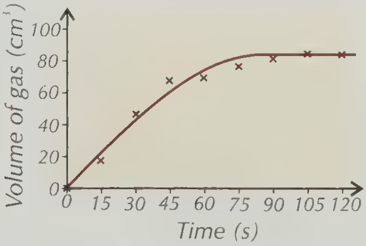


Figure 4: *Scatter graph to show volume of gas evolved against time.*

Scatter graphs and correlation

Correlation describes the relationship between two variables — usually the independent one and the dependent one. Data can show positive correlation, negative correlation or no correlation (see Figure 5).

Learning Objective:

- Be able to plot and interpret suitable graphs from experimental results, including selecting and labelling axes with appropriate scales, quantities and units and measuring gradients.

Specification Reference 1.1.3

Exam Tip
Whatever type of graph you make, you'll only get full marks if you:

1. Choose a sensible scale — don't do a tiny graph in the corner of the paper. Instead, make sure it takes up at least half the space you're given.

2. Label both axes — including units.

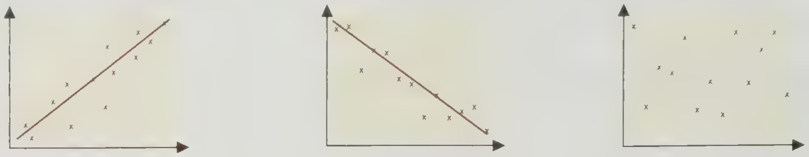
3. Plot your points accurately — using a sharp pencil.

Tip: Use simple scales when you draw graphs — this'll make it easier to plot points.

Tip: A line of best fit should have about half of the points above it and half of the points below. You can ignore any anomalous points, like the one circled in Figure 3.

Tip: Lines of best fit can be curves as well as straight lines — like the example in Figure 4.

Exam Tip
Always check that you've drawn your axes the right way round. The thing you've been changing (the independent variable) goes on the x-axis and the thing you've been measuring (the dependent variable) is on the y-axis.



Positive correlation
As one variable increases the other also increases.

Negative correlation
As one variable increases the other decreases.

No correlation
There is no relationship between the variables.

Figure 5: *Scatter graphs showing positive, negative and no correlation.*

Calculating gradients

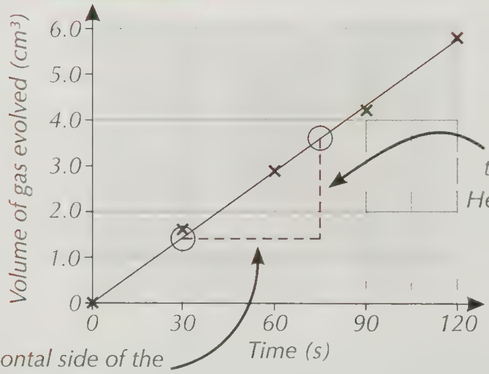
The gradient of a line is how steep it is. It tells you how quickly the y value changes if you change the x value.

gradient = change in y ÷ change in x

To measure the gradient of a straight line, start by picking two points on the line that are easy to read. Draw a vertical line down from one point and a horizontal line across from the other to make a triangle. The vertical side of the triangle is the change in y and the horizontal side is the change in x.

Tip: Gradients are used for working out the rate of reactions, like on pages 186-187.

Example **Maths Skills**



The vertical side of the triangle is the change in y. Here, it's 3.6 – 1.4 = ***2.2 cm³****.*

The horizontal side of the triangle is the change in x. Here, it's 75 – 30 = ***45 s****.*

Figure 6: *Scatter graph showing the volume of gas evolved from a reaction over time.*

The gradient of the graph in Figure 6 tells you the rate at which gas was evolved in the experiment.

Gradient = change in y ÷ change in x = 2.2 ÷ 45 = **0.049 cm³ s⁻¹ (2 s.f.)**

Tip: The easiest points on the line to read are normally the points at which the line passes through the corner of one of the boxes on the graph paper.

If the line of best fit is a curve, then the gradient will be different at different places along the curve. This makes it a bit more complicated to measure the gradient. To find the gradient at a certain point on a curved line of best fit, you first have to draw a tangent to the line at the point where you want to find the gradient. To do this, put a ruler on the graph so that it's just touching the point where you want to find the gradient, and angle the ruler so that there is equal space between the ruler and the curve on either side of the point. Then draw a line along the ruler using a sharp pencil. You can then find the gradient of the tangent in the same way as before.

Example — Maths Skills

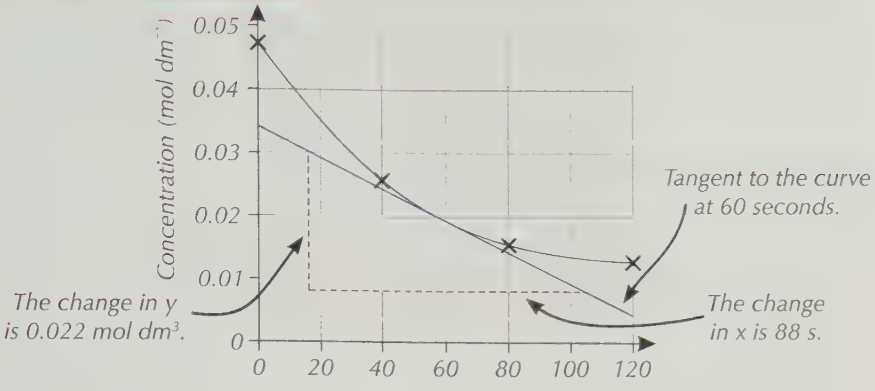


Figure 7: A scatter graph showing the change in concentration of sodium hydroxide in its reaction with 2-bromopentane over time.

The gradient at each point along the curve in Figure 9 tells you what the rate of a reaction is at that point in time. The purple line is the tangent to the curve at 60 seconds. So the rate of the reaction at 60 seconds is equal to the gradient of this tangent.

Gradient = change in y ÷ change in x = 0.022 ÷ 88
= 2.5×10^{-4} mol dm^{-3} s^{-1}

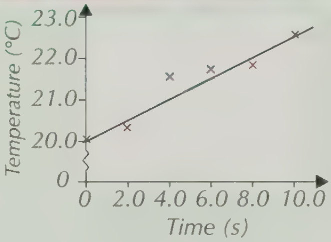
Tip: Always use a ruler and a sharp pencil to draw the tangent to a curve.

Practice Questions — Application

Q1 The graph on the right shows the change in temperature of a reaction mixture in the first ten seconds of the reaction.

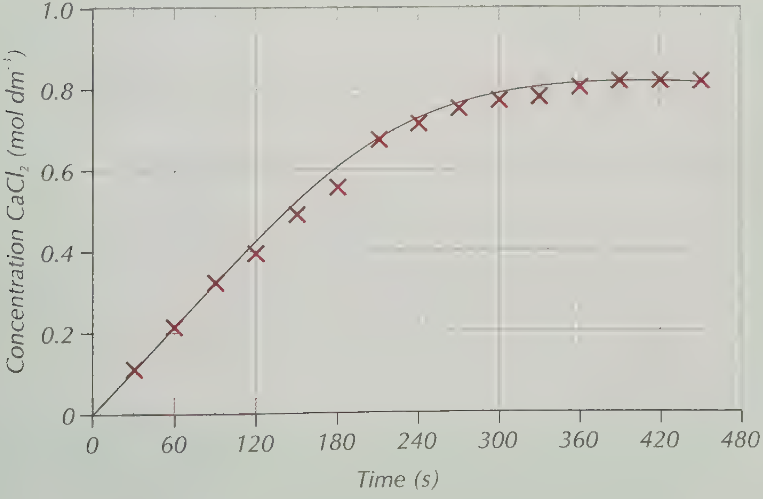
a) Identify any anomalous results.

b) What is the gradient of the graph?



Tip: Remember that anomalous results are ones that don't fit with the other values so are likely to be wrong.

Q2 The graph below shows the change in concentration of $CaCl_2$ in the following reaction: $CaCO_{3(s)} + 2HCl_{(aq)} \rightarrow CaCl_{2(aq)} + H_2O_{(l)} + CO_{2(g)}$.



Calculate the gradient after:

a) 60 seconds b) 180 seconds c) 360 seconds

5. Conclusions and Evaluations

So you planned your experiment, you've run your tests and you've plotted a nice graph. It's not time to put your feet up yet though, you've got a conclusion to write and an evaluation to do.

Learning Objectives:

- Know how to evaluate results and draw conclusions.
- Know how to analyse and interpret qualitative and quantitative experimental results.
- Understand the precision and accuracy of measurements and data, including margins of error, percentage errors and uncertainties in apparatus.
- Be able to identify the limitations in experimental procedures.
- Be able to refine experimental design by suggestion of improvements to the procedures and apparatus.

Specification Reference
1.1.3, 1.1.4

Drawing conclusions

When you look at your graph, you may see that there's a **correlation** between two variables. For example, that as one variable increases so does the other. This could lead you to conclude that increasing one variable causes the other to increase. But this isn't necessarily the case — correlation doesn't always mean causation. Ideally, only two quantities would ever change in any experiment — everything else would remain constant. But in experiments or studies outside the lab, you can't usually control all the variables. So even if two variables are correlated, the change in one may not be causing the change in the other. Both changes might be caused by a third variable.

Example

Some studies have found a correlation between drinking chlorinated tap water and the risk of developing certain cancers. So some people argue that this means water shouldn't have chlorine added. But it's hard to control all the variables between people who drink tap water and people who don't. It could be due to many lifestyle factors. Or, the cancer risk could be affected by something else in tap water — or by whatever the non-tap water drinkers drink instead.

You also need to be sure that the conclusion you draw is supported by the data. This may sound obvious but it's easy to jump to conclusions. Conclusions have to be specific — not make sweeping generalisations.

Example

The rate of an enzyme-controlled reaction was measured at 10 °C, 20 °C, 30 °C, 40 °C, 50 °C and 60 °C. All other variables were kept constant, and the results are shown in Figure 1.

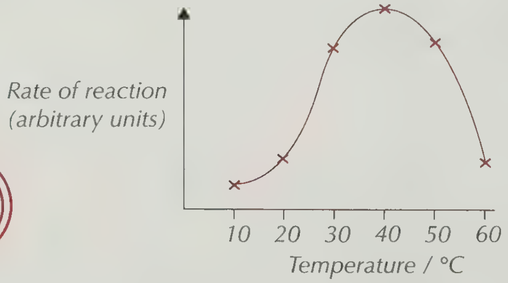


***Figure 1:** Graph to show the effect of temperature on the rate of an enzyme-controlled reaction.*

A science magazine concluded from this data that enzyme X works best at 40 °C. The data doesn't prove this. The enzyme could work best at 42 °C or 47 °C but you can't tell from the data because increases of 10 °C at a time were used. The rate of reaction at in-between temperatures wasn't measured. All you know is that it's faster at 40 °C than at any of the other temperatures tested.

Also, the experiment only gives information about this particular enzyme-controlled reaction. You can't conclude that all enzyme-controlled reactions happen faster at a particular temperature — only this one. And you can't say for sure that doing the experiment at, say, a different constant pressure, wouldn't give a different optimum temperature.

Tip: Watch out for bias too — for instance, a bottled water company might point these studies out to people without mentioning any of the doubts.

Tip: If an experiment really does confirm that changing one variable causes another to change, we say there's a causal link between them.

Tip: Whoever funded the research may have some influence on what conclusions are drawn from the results, but scientists need to make sure that the conclusions they draw are supported by the data.

Evaluations

There are a few terms that you need to understand. They'll be useful when you're evaluating how convincing your results are.

1. Valid results

Valid results answer the original question, using reliable data. For example, if you haven't controlled all the variables your results won't be valid, because you won't be testing just the thing you wanted to.

2. Accurate results

Accurate results are those that are really close to the true answer.

3. Precise results

Precise results can be consistently reproduced in independent experiments. If results are reproducible they're more likely to be true. If the data isn't precise you can't draw a valid conclusion. For experiments, the more repeats you do, and the closer together the data you get, the more precise it is. If you get the same result twice, it could be the correct answer. But if you get the same result 20 times, it's much more likely to be correct. And it'd be even more precise if everyone in the class gets about the same results using different apparatus.

Tip: Precise results are sometimes called reliable results. So, just like precise results, reliable results are repeatable and reproducible, and you can improve the reliability of an experiment by taking repeat readings and calculating a mean.

Uncertainty

Any measurements you make will have uncertainty in them due to the limits to the sensitivity of the equipment you used. For any piece of equipment you use, the uncertainty will be half the smallest increment the equipment can measure, in either direction.

Example — Maths Skills

If you use a weighing scale that measures to the nearest 0.1 g, then the true weight of any substance you weigh could be up to 0.05 g more than or less than your reading. Your measurement has an uncertainty (or error) of ±0.05 g in either direction.

Tip: The ± sign tells you the range in which the true value could lie. The range can also be called the margin of error.

If you're combining measurements, you'll need to combine their uncertainties. For example, if you're calculating a temperature change by measuring an initial and a final temperature, the total uncertainty for the temperature change will be the uncertainties for both measurements added together.

Example — Maths Skills

In a titration using a burette that measures to the nearest 0.05 cm^3, the initial reading is 10.10 cm^3 and the final reading is 19.75 cm^3.

The uncertainty in each reading will be 0.05 $cm^3 \div 2 = \pm 0.025$ cm^3.

So the total uncertainty will be 0.025 cm^3 + 0.025 cm^3 = **±0.05 cm^3**.

Percentage error

You can calculate the **percentage error** of a measurement using this equation:

$$\text{percentage error} = \frac{\text{uncertainty}}{\text{reading}} \times 100$$

Tip: Percentage error is sometimes called percentage uncertainty.

Tip: Percentage error means you can directly compare the degree of error in different measurements as a proportion of the total measurement.

Tip: Equipment will also have an error based on how accurately it has been made. The manufacturers should give you these error values — often they'll be written on the equipment somewhere (see Figure 2).

Examples — Maths Skills

Percentage error of a single measurement

A solution is measured to be 16.5 °C by a thermometer that has graduations every 0.5 °C. This reading will have an uncertainty of $0.5 \div 2 = 0.25$ °C so the percentage error is $\frac{0.25}{16.5} \times 100 = \mathbf{1.5\ \%}$.

Combining percentage errors

A balance that measures to the nearest 0.2 g is used to measure the change in mass of a substance. The initial mass is measured as 40.4 g. The final mass is measured as 22.0 g.

The change in mass is:

$$40.4 - 22.0 = 18.4 \text{ g}$$

The balance measures to the nearest 0.2 g, so each reading has an uncertainty of ±0.1 g. Two readings have been combined, so the total uncertainty is:

$$0.1 \times 2 = 0.2 \text{ g}$$

So for the change in mass, percentage error $= \frac{0.2}{18.4} \times 100 = \mathbf{1.1\%}$

You can reduce errors in your measurements by using the most sensitive equipment available to you. A bit of clever planning can also improve your results. The general principle is that the smaller the measurement, or the larger the increments on your measuring equipment, the larger the percentage error.

Example

If you measure out 5 cm^3 of liquid in a measuring cylinder that has increments of 0.1 cm^3 then the percentage error is $(0.05 \div 5) \times 100 = 1\%$. But if you measure 10 cm^3 of liquid in the same measuring cylinder the percentage error is $(0.05 \div 10) \times 100 = 0.5\%$. Hey presto — you've just halved the percentage error. So the percentage error can be reduced by planning an experiment so you use a larger volume of liquid.

Figure 2: A conical flask where the graduations have an error of 5%.

Types of error

Errors in your results can come from a variety of different sources.

Random errors

Random errors vary — they're what make the results a bit different each time you repeat an experiment. The errors when you make a reading from a burette are random. You have to estimate or round the level when it's between two marks — so sometimes your figure will be above the real one, and sometimes it will be below.

Repeating an experiment and finding the mean of your results helps to deal with random errors. The results that are a bit high will be cancelled out by the ones that are a bit low. So your results will be more precise (reliable).

Systematic errors

Systematic errors are the same every time you repeat the experiment. They may be caused by the set-up or equipment you used. For example, if the 10.00 cm^3 pipette you used to measure out a sample for titration actually only measured 9.95 cm^3, your sample would have been about 0.05 cm^3 too small every time you repeated the experiment.

Repeating your results won't get rid of any systematic errors, so your results won't get more accurate. The best way to get rid of systematic errors is to carefully calibrate any equipment you're using, if possible.

Writing an evaluation

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You may well be asked to evaluate a method for an experiment you or somebody else has carried out. In your evaluation you need to think about anything that you could have done differently to improve your results. Here are some things to think about...

1. You need to consider whether the method gives **valid** results. This includes deciding whether the data you collected addressed the aim of the experiment and whether you collected enough data to support your conclusions. You should also think about whether you controlled all the necessary variables to make it a fair test.
2. Next think about how you could have improved the **accuracy** of your results. You should think about whether the apparatus you used was an appropriate scale for your measurements (not too big or too small) and whether you could have used more sensitive equipment to reduce the random errors and uncertainty of your results.
3. Finally, evaluate how **precise** your results are. For most experiments you should have repeated your tests. If so, you should look at whether the results you got were similar, and if you didn't you should consider whether you should repeat your experiment in the future.

Exam Tip
If you think there is a problem with a method, try and explain how you could solve it as well as just stating what it is.

Practice Questions — Application

Q1 a) What is the uncertainty of a measurement made with a measuring cylinder that has graduations every 2.0 cm^3?

b) What is the percentage error of a measurement of 8.0 cm^3 made with the measuring cylinder in part a)?

c) Suggest how you could reduce the percentage error of the measurement in b).

Q2 A student is investigating the rate at which hydrogen gas is evolved in the reaction between magnesium and hydrochloric acid. She repeats her experiment three times using the following method:

1. Measure out 25.0 cm^3 0.1 mol dm^{-3} hydrochloric acid in a measuring cylinder. Put it in a conical flask fitted with a bung connected to a gas syringe.
2. Put one spatula of magnesium chips into the conical flask, replace the bung and start the timer.
3. Record the volume of gas evolved every five minutes until the reaction is complete.

a) Will the student's results be valid? If not, describe what the student should do instead.

b) The student finds that the volume of gas increases between her readings at five and ten minutes, but there is no change between ten and fifteen minutes, indicating that the reaction is complete. How could the student improve the method to give more accurate results about how the rate changes over the course of the reaction?

Section Summary

Make sure you know...

- The steps involved in planning an experiment.
- The difference between an independent and a dependent variable, and how to identify other variables that will need to be controlled during an experiment.
- The different types of data you might be required to collect in an experiment.
- How to choose what data you should collect in an experiment.
- That the equipment used in an experiment needs to be of the right size, scale and sensitivity.
- How to draw basic laboratory equipment when drawing a diagram of the set-up for an experiment.
- The importance of carrying out a risk assessment for an experiment.
- How to write a detailed method for an experiment.
- How to measure masses of solids, and volumes of liquids and gases, and how to reduce transfer errors associated with moving substances between different containers.
- How to measure the temperature of a substance.
- How to reduce subjectivity when making qualitative measurements.
- What the organic techniques reflux, distillation and separation may be used for.
- How to organise your results into a table of data.
- How to identify anomalous results in your data.
- How to calculate a mean from a data set.
- How to correctly use units and significant figures in your data.
- The different types of graphs you can use, and which one to use for a given set of data.
- That two variables may have a positive, a negative or no correlation.
- How to find gradients from scatter graphs.
- That correlation between variables doesn't always mean that a change in one causes a change in the other, as a third variable may be causing the change.
- How to draw conclusions that are properly backed up by your data.
- What valid, accurate and precise results are.
- How to calculate the uncertainty and percentage error of a measurement.
- How to identify possible errors in a method.
- How to evaluate a method and suggest ways in which it could be improved.

Exam-style Questions

1 What is the error associated with a measurement of 2.45 g on a set of scales that measures to the nearest 0.05 g?

A ±0.025 g

B ±0.05 g

C 2.04%

D 1.02%

(1 mark)

2 The table below shows the results of an experiment to see how long it takes for a reaction to be completed at 30 °C. The experiment was repeated four times.

Temperature (°C)	Time until reaction is complete (s)			
	Repeat 1	Repeat 2	Repeat 3	Repeat 4
30	410	450	398	406

What is the correct value of the mean time taken for the reaction to be completed?

A 416 s

B 422 s

C 405 s

D 408 s

(1 mark)

3 A student carried out an experiment to find the temperature change of the reaction between 2 g calcium carbonate and 20 ml of 2.0 mol dm^{-3} hydrochloric acid. She measured the temperature of the hydrochloric acid, then added the calcium carbonate and allowed the reaction to run to completion. The reaction was complete when gas was no longer evolved from the reaction vessel. After the reaction had finished, the student took a final temperature measurement and calculated the overall temperature change. The student's result for the total temperature change of the reaction was less than she expected it to be. Which of the following things the student did could have contributed to the temperature change being less than expected?

Action 1: The student used some water to wash the calcium carbonate from the weighing container into the reaction vessel.

Action 2: The student added the calcium carbonate to the reaction vessel two minutes after taking the initial temperature reading.

Action 3: The student left the reaction vessel for ten minutes after the reaction had finished before taking the final reading.

A Only action 3

B Actions 1, 2 and 3

C Actions 1 and 2

D Actions 1 and 3

(1 mark)

4 A student makes a standard solution by weighing out a solid and adding it to a volumetric flask. He washes the weighing vessel with some water and pours this water into the volumetric flask. He fills the flask with water until the top of the meniscus is level with the line on the flask. He then puts a cap on the flask and shakes it.

(a) Identify and correct what the student has done wrong in the above method.

(1 mark)

(b) Why does the student wash the weighing vessel into the volumetric flask?

(1 mark)

(c) Why does the student shake the flask?

(1 mark)

5 When calcium carbonate is heated, it decomposes to form a solid and a gas. The table below shows the results of an experiment in which a student investigated the total volume of gas produced by different sized samples of calcium carbonate when heated vigorously.

Mass (g)	Volume gas (cm^3)
0.020	4.65
0.040	9.70
0.060	14.45
0.080	16.20
0.100	24.65

(a) Draw a graph of these results, including a line of best fit.

(3 marks)

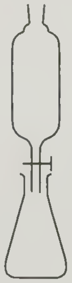
(b) Describe any correlation in these results.

(1 mark)

(c) The gradient of the graph tells you how many cm^3 of gas each gram of calcium carbonate will produce. Calculate the gradient of the graph.

(2 marks)

6 A student carries out an experiment to synthesise the organic compound hexene from hexan-2-ol. Once synthesised, hexene needs to be purified from the reaction mixture. The first step in the purification uses the apparatus in the diagram below.



(a) Name the two pieces of equipment in the diagram above.

(2 marks)

(b) What is the apparatus in the diagram used for?

(1 mark)

PRACTICAL SKILLS

Practical Skills for the Practical Endorsement

What is the Practical Endorsement?

The Practical Endorsement is assessed slightly differently to the rest of your course. Unlike the exams, you don't get a mark for the Practical Endorsement — you just have to get a pass grade. The Practical Endorsement is split into twelve categories, called Practical Activity Groups (PAGs). Each PAG covers a variety of practical techniques, for example, measuring mass or heating under reflux. In order to pass the Practical Endorsement, you'll have to carry out at least one experiment for each PAG, and demonstrate that you can carry out each of the required techniques. You'll do the experiments in class, and your teacher will assess you as you're doing them.

This section takes you through some of the techniques you'll meet during your A Level course, as well as tips for keeping an accurate record of the experiments you've carried out for your Practical Endorsement.

Tip: Throughout this book, experiments and skills that you could use for your Practical Endorsement are marked with a big PAG stamp, like this one:

PRACTICAL ACTIVITY GROUP 4

1. General Practical Skills

The way you do an experiment is important. You may be given a method, or you may have to plan it yourself. It's important that you follow all the steps in a method — this ensures that you work safely, and also that your results will be precise.

Tip: Experiments are often used to test scientific theories to see if they are true in a practical context.

Solving problems in a practical context

Practical experiments are used to solve problems or test whether a theoretical model works in a practical setting. If you're given a method to follow for an experiment, you should carry out each step, as described, in the correct order.

It's possible you'll be given a problem and asked to solve it using your own knowledge. There's loads of information about how to plan and carry out experiments correctly on pages 5-14 — take a look back if it's all a bit hazy. Here's a quick round-up of some of the things you'll need to think about when you plan an experiment:

- First, identify the aim of your experiment.
- Next, work out how to achieve the aim. You'll often need to identify a variable that you'll change (the independent variable) and the variable you'll measure (the dependent variable) in order to gather data that meets the aim of your experiment.
- Identify all the variables that will need to be controlled during your experiment, and how to control them.
- Think about how to make your data as precise and accurate as possible. This could include repeating your experiment a number of times, or choosing equipment with a scale that has the right sensitivity for the data you're trying to collect.

Tip: Variables include things like temperature, time, mass, volume and colour.

Tip: Precise results are reproducible and repeatable. Accurate results are close to the true value.

Recording observations and analysing data

Once your experiment is planned, you can carry it out, working carefully to make sure your results are precise. There's loads of information about how to carry out some general techniques you may come across on pages 33-38, and other techniques are covered as they come up during the course. You'll also have already come across some techniques on pages 11-14. As you carry out your experiment, you should record your results in a well laid-out table, leaving space for any data analysis you might want to do later. This may include finding averages or using your table of data to draw a graph of your results.

Tip: If you need more information about analysing data, including the maths you'll need to know and how to draw and interpret graphs, have a look back at Module 1 — it's all covered there.

Uncertainties and error

An important part of your data analysis is to work out the percentage error and uncertainties in the apparatus you've used — look back at pages 21-22 for more information on these.

Uncertainty

For any piece of equipment you use, the uncertainty will be half the smallest increment the equipment can measure, in either direction.

Percentage error

You can calculate the percentage error of a measurement using this equation:

$$\text{percentage error} = \frac{\text{uncertainty}}{\text{reading}} \times 100$$

Tip: Uncertainty tells you how much the value of a measurement could be out by. Percentage error gives this uncertainty as a percentage of the measurement you made.

Tip: In science, error doesn't mean things have gone wrong — instead it's a measure of how different your results could be to their true value based on how sensitive the equipment you used is.

Conclusions and evaluations

When you've collected and analysed your data, it's time to wrap up your experiment with some conclusions and an evaluation (see pages 20-23). Conclusions explain what your results showed. They need to be supported by the data you collected, and shouldn't make sweeping generalisations. Sometimes, you'll be looking to see if there is a correlation between two variables, but you should be cautious before claiming that the change in one is what causes the change in the other — there may be another factor that is causing both variables to change.

An evaluation is a chance for you to look at what you did and think about how you could have improved your method to improve the validity, accuracy and precision of your results. You should consider how well your results address the original aim of your experiment, how you could reduce errors in your results, and whether you need to repeat your experiment further to show your results can be reproduced.

Tip: If two variables are correlated, then as one of the variables changes, so will the other.

Tip: Some results won't fit the trend of your data at all — these are anomalous results, and you tend to get them if something went wrong as you carried out your experiment. You should ignore anomalous results when calculating averages or drawing lines of best fit.

2. Working Safely

When you do an experiment, you need to carry out a risk assessment and work safely at all times. This reduces the risk of anyone being hurt.

Risks and hazards

HOW SCIENCE WORKS

Many chemistry experiments have risks associated with them. These can include risks associated with the equipment you're using, such as the risk of burning from a hot plate, as well as risks associated with chemicals. When you're planning an experiment, you need to identify all the hazards and what the risk is from each hazard. This includes working out how likely it is that something could go wrong, and how serious it would be if it did go wrong. You then need to think of ways to reduce these risks. Any hazardous chemicals you use should come with a list of dangers associated with them — this can be found on the bottle they come in, or looked up on something called a Material Safety Data Sheet.

Hazard word	Potential harm	Examples of how to reduce the risk
Corrosive	May cause chemical burns to tissues such as skin and eyes.	Use as little of the substance as possible. If the chemical is a solution, use it in low concentrations. If the chemical is a gas, carry out the experiment in a fume cupboard. Wear a lab coat, goggles and gloves when handling the chemical.
Irritant	May cause inflammation and discomfort.	Use as little of the substance as possible. If the chemical is a solution, use it in low concentrations. If the chemical is a gas, carry out the experiment in a fume cupboard. Wear a lab coat, goggles and gloves when handling the chemical.
Flammable	May catch fire.	Keep the chemical away from any naked flames. If you have to heat it, use a water bath, an electric heater or a sand bath instead of a Bunsen burner.
Toxic	May cause illness or even death.	Use as little of the substance as possible. If the chemical is a solution, use it in low concentrations. If the chemical is a gas, carry out the experiment in a fume cupboard. Wear a lab coat, goggles and gloves when handling the chemical.
Oxidising	Reacts to form oxygen, so other substances may burn more easily in its presence.	Use as little of the substance as possible. Use it in solution rather than as a solid powder. Use in clean, well-ventilated areas. Keep away from combustible materials, such as wood or paper.

Figure 1: *Some common types of hazard and how to reduce the risks they present.*

Tip: A hazard is anything that has the potential to cause harm or damage. The risk associated with that hazard is the probability of someone (or something) being harmed if they are exposed to the hazard.

Tip: The CLEAPSS® website has a database with details of the potential harm lots of the hazardous chemicals you're likely to come across could cause. It also has student safety sheets, and your school or college may have CLEAPSS® hazcards® you can use. These are all good sources of information if you're writing a risk assessment.

Tip: This isn't a comprehensive list of all the types of hazard you may encounter — just some of the more common ones.

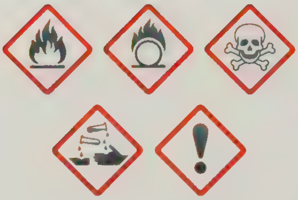


Figure 2: *The hazard symbols for flammable (top left), oxidising (top middle), toxic (top right), corrosive (bottom left) and irritant (bottom right).*

Example

A student plans to carry out an experiment to synthesise the ester propylethanoate using the following procedure:

- Add some propan-1-ol and concentrated ethanoic acid to a test tube containing concentrated sulfuric acid.
- Gently heat the mixture for 1 minute.
- Cool the mixture.
- Pour the mixture into a solution of sodium carbonate and mix to neutralise any remaining acid.

This experiment involves hazards in both the procedure and the chemicals used. For example, one hazard in the procedure comes from heating. The risks associated with the chemicals in the experiment are summarised in the table below:

Hazard	Type of hazard	Ways to reduce the risk
Propan-1-ol	Flammable	Keep away from naked flames — carry out the experiment using a water bath to heat the reaction mixture.
	Irritant	Use as little propan-1-ol as possible. Wear a lab coat, goggles and gloves when handling it.
Concentrated ethanoic acid	Corrosive	Use as little concentrated ethanoic acid as possible. Wear a lab coat, goggles and gloves when handling it.
Concentrated sulfuric acid	Corrosive	Use as little concentrated sulfuric acid as possible. Wear a lab coat, goggles and gloves when handling it.
Sodium carbonate solution	Irritant	Use as little sodium carbonate solution as possible, in a low concentration. Wear a lab coat, goggles and gloves when handling it.

Figure 3: *Chemical hazards in an experiment to synthesise propylethanoate.*

To reduce the risk of being burnt by any equipment, you shouldn't touch the apparatus whilst it is being heated. You should use tongs to remove the test tube from the heating apparatus and allow it to cool completely before continuing with the experiment.

The procedure can now be rewritten, taking into account the steps that should be taken to reduce the risks in this experiment:

- Add 1 cm^3 propan-1-ol and 1 cm^3 concentrated ethanoic acid to a test-tube containing 0.5 cm^3 concentrated sulfuric acid.
- Gently heat the mixture in a water bath for 1 minute.
- Remove the test tube from the water bath using tongs, and leave it in a test tube rack on a heat-proof mat to cool.
- Pour the mixture into 5 cm^3 of sodium carbonate solution and mix.

Tip: Esters are organic compounds made by reacting carboxylic acids with alcohols. There's more about how to synthesise them and how they react on pages 462-464.

Tip: The hazard symbols in Figure 2 are quite new, so you may come across the old-style ones on bottles in your laboratory. The symbols are very similar, but they're in orange squares instead of red and white diamonds (see Figure 4).

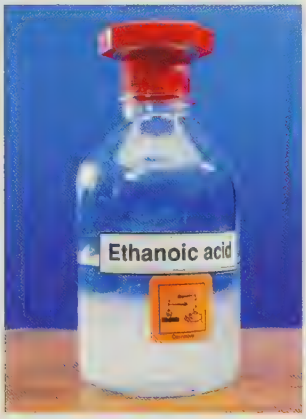


Figure 4: *A bottle of ethanoic acid with a 'corrosive' hazard symbol.*

Tip: The risk associated with a solution might change depending on how concentrated it is. So whilst concentrated sulfuric acid is corrosive, dilute sulfuric acid is an irritant.

3. Keeping Scientific Records

When you carry out experiments, it's important to keep records of everything you do. The records should be detailed and clear enough that a complete stranger would be able to read them and understand what you did.

Records of scientific experiments

Throughout your A Level Chemistry course, you should keep a record of all the experiments you carry out, the results you obtain and the solutions to any data analysis you do. This could be done in a physical lab book, or kept in folders on a computer. However you choose to keep your records, the information for each experiment should include:

- The aim of the experiment.
- A detailed method for how you carried out the experiment, including the quantities of all the chemicals and any safety precautions you had to take.
- The results of your experiment, clearly set out in a table. The results may be hand-written, or a print-out of data collected by a data logger.
- Any other important observations you made whilst carrying out your experiment, for example, anything that went wrong or anything you did slightly differently from how it was described in the method.
- The solutions to any analysis you did on your results, or any graphs drawn using your results. These should be clearly labelled to show what analysis has been done or what graph has been drawn.
- Citations of any references you used.

Tip: Try to keep all your lab reports in the same place — write them in the same book, or keep them in the same folder on your computer. That way you'll know where everything is.

Tip: You'll have already learned about making observations, recording data and analysing your results in Module 1, so take a look back there if you need a reminder.

Sources of information

PRACTICAL ACTIVITY GROUP 12

It's possible you'll have to do some research to find out information before you get started with an experiment. Useful sources of information include:

Websites

Using the Internet for research is really convenient, but you have to be slightly wary as not all the information you find will be true. It's hard to know where information comes from on forums, blogs and websites that can be edited by the general public, so you should avoid using these. Websites of organisations such as the Royal Society of Chemistry and the National Institute of Standards and Technology (NIST) provide lots of information that comes from reliable scientific sources. To decide whether a website gives reliable information, think about the following things:

- Who has written the information — was it a scientist, a teacher, or just a member of the public?
- Whether or not anyone will have checked the source — articles on websites for scientific organisations will have people reading through the information and checking all the facts. Information on forums or blogs is likely to have been written by an individual, and won't necessarily have been thoroughly checked.
- What the purpose of the website is — if it's a website all about Chemistry, then it's likely whoever has written it will know quite a lot. If it's a website where you can also find out how to make a plant pot from an old teacup and some PVA glue, then the depth and quality of the information may not be enough.

Tip: If you're unsure whether the information on a website is true or not, try and find the same piece of information in a different place. The more sources you can find for the information, the more likely it is to be correct.

Textbooks

Your school or public library is likely to have textbooks covering specific areas of Chemistry in a lot of detail.

Tip: Scientific papers are checked by other scientists who are experts in the subject of the paper. This is called peer review (see page 2).

Scientific papers

You can find papers in online catalogues, such as SciFinder or PubMed, as well as in journals that are often available in public libraries.

The source you do your research from needs to give the right level of information. It's no good trawling through a scientific paper if you're just looking for the boiling point of a compound — the information will be far too detailed, and you'll probably end up wading through lots of complicated information that you don't need to understand. Equally, if you're researching the theory behind an experiment, you want a source that gives enough detail. A GCSE textbook will probably be too simplistic — you're better off finding a book that deals specifically with the subject in a library instead.

Using references and making citations

PRACTICAL ACTIVITY GROUP 12

It's going to sound obvious, but when you're using the information that you've found during your research, you can't just copy it down word for word. Any data you're looking up should be copied accurately, but you should rewrite everything else in your own words.

When you've used information from a source, you need to cite the reference properly. Citations allow someone else to go back and find the source of your information. This means they can check your information and see you're not making things up out of thin air. Citations also mean you've properly credited other people's data that you've used in your work.

Citations for each piece of information may include the title of the book, paper or website where you found the information, the author and/or the publisher of the document and the date the document was published.

Tip: There are lots of slightly different ways of referencing sources, but the important thing is that it's clear where you found the information.

Examples

The boiling point of butan-1-ol is 390.6 K. (http://webbook.nist.gov/chemistry)

The boiling point of butan-1-ol is 390.3 K. (Harrison R.D., Ellis H; Nuffield Advanced Science Book of Data Revised Edition; 1984)

4. Practical Techniques

This section is an introduction to some of the techniques you'll be expected to know for A Level Chemistry. There'll be plenty of others covered in more detail as they crop up throughout the book.

Making measurements

Almost every experiment you carry out in Chemistry involves some sort of measurement. Some measurement techniques were already outlined on pages 11-12. These included measuring mass, volumes of liquids and gases, and temperature. During your A Level course, you may also need to measure the pH of a solution.

Tip: Make sure you do a risk assessment before you carry out any of the techniques in this topic.

Measuring pH

PRACTICAL ACTIVITY GROUP 11

The pH of a solution is a measure of how acidic or basic it is. There's more than one way of measuring this — you can use pH charts, pH meters or pH probes.

pH charts

Universal indicator is a substance that changes colour according to the pH of a solution. A pH chart tells you what colour Universal indicator will be at different pHs (see Figure 1). So, if you add a few drops of Universal indicator to a solution, you can compare the resulting colour to a pH chart and determine the pH of the solution. pH charts are good for giving a rough value of the pH of the solution, but since the colour of a solution is a qualitative observation (it's based on opinion), the data won't be accurate or precise.

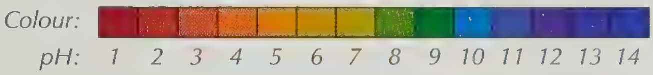


Figure 1: *The pH chart of Universal indicator*

pH meters

A pH meter is an electronic gadget that can be used to give a precise and accurate value for the pH of a solution (see page 356). They are made up of a probe attached to a digital display. The probe is placed in the solution, and the pH reading is shown on the display.

pH probes on a data logger

A pH probe can be attached to something called a data logger. A data logger could be a piece of software on a computer or tablet. It records the pH readings from the pH probe and stores them so you can look back at them later. This makes them useful for experiments where you're measuring how pH changes, as the data logger will record the results, meaning you don't have to write them down separately. You may need to print the results once the experiment is complete, so you can keep a record of them in your lab book.

Tip: Organic compounds are generally flammable, so you might use these methods for heating them when carrying out tests for organic functional groups (see pages 510-513).

Heating substances

PRACTICAL ACTIVITY GROUP 7

Many chemical substances are flammable, so are at risk of catching fire if they're heated with a naked flame, e.g. with a Bunsen burner. Luckily, there are a number of other techniques you can use to heat a reaction mixture.

Electric heaters

Electric heaters are often made up of a dish of metal that can be heated to a specified temperature. The reaction vessel is placed on top of the hot plate (see Figure 2). The mixture is only heated from below, so you'll usually have to stir the reaction mixture to make sure it's heated evenly.

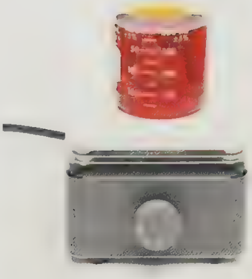


Figure 2: *An electric heater.*

Water baths

A water bath is a container filled with water that can be heated to a specific temperature (Figure 3). You place the reaction vessel in the water bath until the reaction mixture is completely submerged. The mixture will then be warmed to the same temperature as the water. As the reaction mixture is surrounded by water, the heating is very even. However, water boils at 100 °C, so you can't use a water bath to heat the reaction mixture to a higher temperature than this.

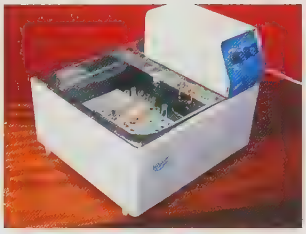


Figure 3: *A water bath.*

Sand baths

Sand baths are similar to water baths, but the container is filled with sand. Sand can be heated to a much higher temperature than water, so sand baths are useful for heating reaction mixtures to temperatures above 100 °C.

Acid-base titrations

PRACTICAL ACTIVITY GROUP 2

Titrations are used to find the concentration of an unknown solution. In acid-base titrations, the concentration of an acid can be determined by finding how much base of a known concentration is required to neutralise a given volume of it, or vice versa. The mixture is shown to be neutralised by the colour change of an **indicator**. The indicator you use for a particular titration needs to change colour at a pH that falls in the range in which the pH of the mixture changes rapidly upon addition of a small amount of acid or base.

Tip: Titrations between weak acids and weak bases can't be carried out using an indicator, as there's no clear end point.

Strength of acid	Strength of base	Range in which pH changes rapidly
Strong	Strong	2-12
Strong	Weak	2-8
Weak	Strong	8-11
Weak	Weak	Only gradual change

Two common indicators are methyl orange and phenolphthalein. Methyl orange changes colour from red to yellow as the pH changes from about 3.1-4.4. So it's suitable as an indicator in titrations between strong acids and either weak or strong bases. Phenolphthalein changes colour from colourless to purple as pH changes from about 8.3-10, so you can use it in titrations between strong or weak acids and strong bases.

Measuring rates of reactions

There are two common ways of measuring how the rate of reaction changes when you vary the concentration of one of the reactants.

1. Continuous monitoring

PRACTICAL ACTIVITY GROUP 9

Continuous monitoring experiments show you how the rate of a reaction changes over the course of the entire reaction. They're done by taking regular measurements of the amount of one of the reactants or products over the course of the reaction. For example, if a gas is produced you could measure the volume of gas formed at regular intervals, or if there is a colour change you could use colorimetry to measure how the absorbance of a particular frequency of light changes over time. The results can be used to plot a graph of the variable you measured against time, for example, a volume-time graph or a concentration-time graph. The rate of the reaction at any point is given by the gradient of these graphs at that point, with units of the variable you measured against time (for example, $cm^3\ s^{-1}$ for a volume-time graph or $mol\ dm^{-3}\ s^{-1}$ for a concentration-time graph).

Tip: There's loads more about finding the rate of a reaction from a concentration-time graph on pages 293-294.

Sometimes, you may have collected data such as volume or pH, and want to convert it into concentration in order to plot a concentration-time graph. This can be done with a few calculations, such as on pages 290-291. You may also have found the change in concentration of one of the products, and want to determine how the concentration of one of the reactants changes over time. You can do this using your information about the product formation and the reaction equation. There's more detail on how to do this on page 291.

Tip: The order of a reaction with respect to a reactant tells you how much the rate will change if you vary the concentration of that reactant (see page 299).

2. Initial rates

PRACTICAL ACTIVITY GROUP 10

The initial rates method is used to investigate the order of a reaction with respect to each of the reactants. You carry out a series of experiments that let you work out the rate at the beginning of the reaction for different starting concentrations of one reactant. For example, you could measure the volume of gas that's produced in the first 30 seconds of a reaction for four different starting concentrations of one reactant.

You can also use a **clock reaction** to give you an approximation of the initial rate of the reaction. Here, at a set concentration of one of the products, a visual change such as a colour change is seen in the reaction mixture. You carry out a series of experiments, each with a different starting concentration of one of the reactants, and measure the time taken for this change to occur.

Once you've carried out these experiments at different reactant concentrations, you can work out the initial rate for each reaction and plot a graph of rate against the initial concentration of the reactant you investigated. The numerical data you've got and the shape of the graph both tell you the order of the reaction with respect to the reactant you've investigated.

Tip: Orders of reactions and initial rates experiments are quite hard to get your head around, so don't worry if it all seems a bit strange at the moment. There's loads more information in Module 5 on pages 295-301.

Tip: The iodine clock reaction is the most famous clock reaction. See page 297 for more detail.

Setting up electrochemical cells

PRACTICAL ACTIVITY GROUP 8

Electrochemical cells use redox reactions to generate electricity. For example, batteries are electrochemical cells. You can make your own electrochemical cell from two half cells — metal electrodes dipped in separate flasks containing a solution of their own metal ions. The electrodes are connected by a wire that runs though a voltmeter, which can be used to measure the voltage of the cell. To complete the circuit, the two flasks are connected by a salt bridge — normally a strip of paper dipped in a solution of inert ions, such as KNO_3. The salt bridge allows ions to pass between the half cells, but doesn't interfere with the reaction happening at either electrode.

Tip: There's loads more about electrochemical cells and the reactions that occur at the electrodes in Module 5 Section 5.

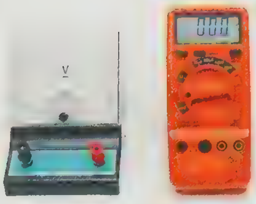


Figure 4: *An analogue and a digital voltmeter.*

Tip: Measuring the voltage of an electrochemical cell tells you the difference in reduction potentials between the two metals at each of your electrodes.

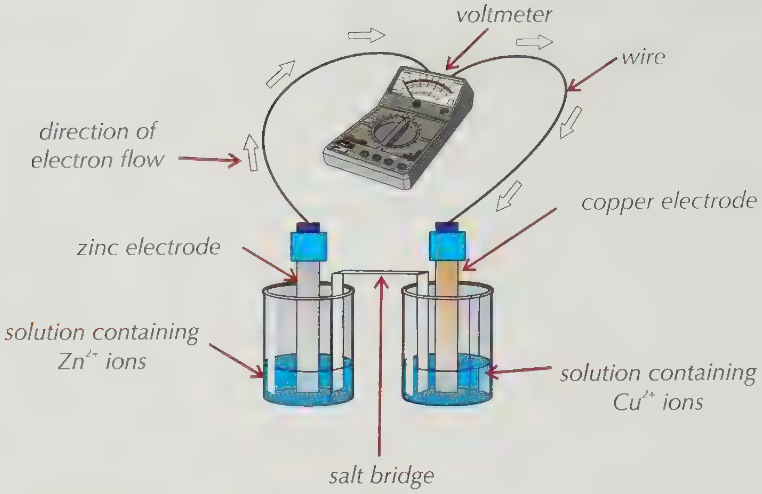

voltmeter
wire
direction of electron flow
copper electrode
zinc electrode
solution containing Zn^{2+} ions
solution containing Cu^{2+} ions
salt bridge

Figure 5: *An electrochemical cell made up of zinc and copper electrodes.*

Organic techniques

PRACTICAL ACTIVITY GROUP 6

Some techniques for synthesising and purifying organic liquids were covered on pages 13-14. You also need to know how to synthesise and purify an organic solid. The synthesis techniques are the same, but there are some more techniques you need to know about for purifying organic solids — filtration and recrystallisation, for example.

Filtration

PRACTICAL ACTIVITY GROUP 6

Filtration is used to separate a solid from a liquid.
There are two types of filtration you need to know about:

Tip: There's more detail about these organic techniques on pages 498-500.

1. Filtration under reduced pressure

Filtration under reduced pressure is normally used when you want to keep the solid and discard the filtrate. You use a piece of equipment called a Büchner funnel — a flat-bottomed funnel with holes in the base. The Büchner funnel is attached to the top of a side-arm flask, which is secured with a stand-and-clamp to stop it from falling over. The side-arm flask is attached to a vacuum line, which, when it is switched on, causes the flask to be under reduced pressure.

Here's how you carry out the filtration:

- Place a piece of filter paper, slightly smaller than the diameter of the funnel, on the bottom of the Büchner funnel so that it lies flat and covers all the holes.
- Wet the paper with a little solvent, so that it sticks to the bottom of the funnel, and doesn't slip around when you pour in your mixture.
- Turn the vacuum on, and then pour your mixture into the funnel. As the flask is under reduced pressure, the liquid is sucked through the funnel into the flask, leaving the solid behind.
- Rinse the solid with a little of the solvent that your mixture was in. This will wash any of the original liquid from the mixture (and so any soluble impurities) that has stayed on your wet, solid crystals into the flask, and leave you with a more pure solid.
- Disconnect the vacuum line from the side-arm flask and then turn off the vacuum.
- The solid will be a bit wet from the solvent, so leave it to dry completely.

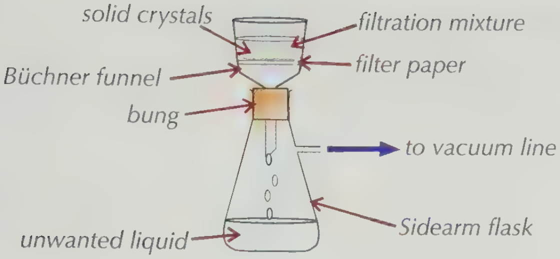


Figure 6: *Apparatus for filtration under reduced pressure.*

2. Filtration using fluted filter paper

Filtration using fluted filter paper is normally used when you want to keep the liquid (the filtrate) and discard the solid. For example, it can be used to remove the solid drying agent from the organic layer of a liquid that has been purified by separation. A piece of fluted filter paper is placed in a funnel that feeds into a conical flask. The mixture to be separated is poured gently into the filter paper. The solution will pass through the filter paper into the conical flask, and the solid will be trapped. A pure sample of the solvent present in the solution can be used to rinse the solid left in the filter paper. This makes sure that all the soluble material has passed through the filter paper and collected in the conical flask.

Tip: If you're doing a filtration using fluted filter paper, take care not to fill the funnel above the top of the filter paper when you're pouring in your mixture.

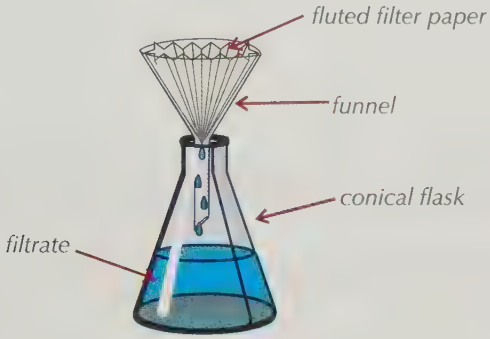
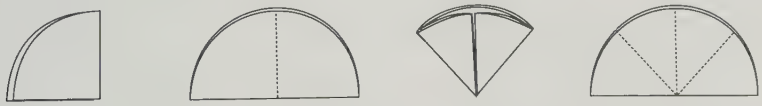


Figure 7: *Filtration using fluted filter paper.*

Tip: Fluted filter paper is a cone with a concertinaed edge. The concertina gives the paper a greater surface area than if the paper were smooth, so the solution is filtered faster.

Filter paper normally comes as a flat disc. To make fluted filter paper, follow the steps in Figure 8.

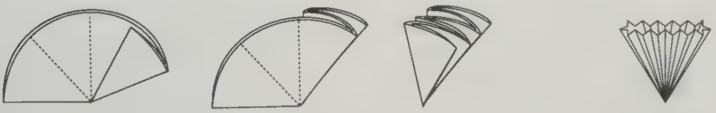


1. Fold the paper in half, then in quarters.

2. Unfold the paper so it's in half.

3. Fold each side into the centre.

4. Unfold the paper again so that it's in half.



5. Concertina the paper, using the folds as guidelines.

6. Unfold the paper, and make it into a cone.

Figure 8: *Making fluted filter paper.*

Tip: The solvent you choose for a recrystallisation is important — see page 499 for more on this and more information on recrystallisation.

Recrystallisation

PRACTICAL ACTIVITY GROUP 6

Recrystallisation is used to purify an organic solid. A solvent is chosen in which the organic product is soluble when the solvent is hot, and insoluble when the solvent is cold. The impure solid is dissolved in a minimal amount of hot solvent. The solution is then left to cool, and the pure product should crystallise out of the solution whilst any soluble impurities stay in solution. The pure crystals can be removed from the solvent containing the impurities by filtration under reduced pressure.

Testing the purity of an organic solid

PRACTICAL ACTIVITY GROUP 6

The purity of an organic solid can be assessed in a couple of different ways.

Tip: See page 500 for more detail on how to measure the melting points of organic solids.

1. Melting point

If you measure the melting point of a pure solid, you should get the same value as stated in a data book. The range in temperature over which the solid melts should also be very small. An impure solid will have a melting point that is lower than the recorded value, and it will melt over a wider range in temperature. So, you can determine how pure a solid sample is by measuring its melting point and comparing it to the recorded value. You can find the melting point of a solid using a piece of equipment called a melting point apparatus. The lower the melting point is than the standard value, and the greater the range of the melting point, the less pure the solid is.

Tip: Chromatography plates can be made of paper or they might be a piece of glass or plastic coated with a thin solid layer such as silica gel or aluminium powder.

2. Thin layer or paper chromatography

Thin layer or paper chromatography separates a liquid mixture into its component parts based on how well each component dissolves in a particular solvent. Each component in a mixture will show up as a spot at a different point on a chromatography plate. By looking at how many points are on a chromatography plate, you can determine how many components are in your mixture, and so how pure your sample is.

In a chromatography experiment, a solid is dissolved into a solution, and a drop of the mixture is put near the bottom of a plate. The plate is then placed in a beaker containing a small amount of a solvent, so that the solvent sits below the spot of mixture. The solvent moves slowly up the plate, and the components of the mixture move with it at different speeds depending on how well they dissolve in the solvent. At the end of the experiment, each component part of the mixture will be separated into spots positioned at different places along the plate.

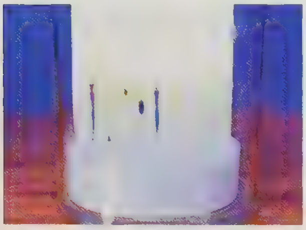


Figure 9: Using paper chromatography to separate the components of different coloured inks.

Tip: See pages 514-515 for more on chromatography.

Module 2 Section 1: Atoms and Moles

1. The Atom

Atoms are the basis of all of chemistry. You learned about them at GCSE and they crop up again here. They're super important.

Learning Objectives:

- Be able to describe atomic structure in terms of the number of protons, neutrons and electrons for atoms and ions given the atomic number, mass number and any ionic charge.
- Know that isotopes are atoms of the same element with different numbers of neutrons and different masses.

Specification Reference 2.1.1

The structure of the atom

All elements are made of **atoms**. Atoms are made up of 3 types of particle — **protons**, **neutrons** and **electrons**. Figure 1 shows how they are arranged in the atom.

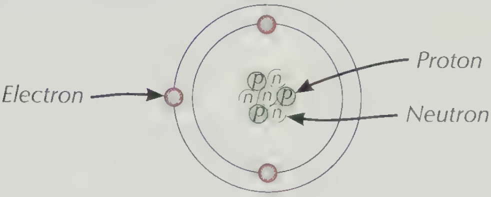


Figure 1: *The atom.*

Electrons have 1– charge. They whizz around the nucleus in orbitals. The orbitals, and the spaces between them, take up most of the volume of the atom. Most of the mass of the atom is concentrated in the **nucleus**. The diameter of the nucleus is rather titchy compared to the whole atom. The nucleus is where you find the protons and neutrons. The mass and charge of these subatomic particles are really small, so relative mass and relative charge are used instead. The mass of an electron is negligible compared to a proton or a neutron — it's about 2000 times smaller. Figure 2 shows the relative masses and charges of protons, neutrons and electrons.

Subatomic particle	*Relative mass*	*Relative charge*
Proton	*1*	*1+*
Neutron	*1*	*0*
Electron, e^-	$\frac{1}{2000}$	*1–*

Figure 2: *Relative masses and relative charges of subatomic particles.*

Nuclear symbols

You can figure out the number of protons, neutrons and electrons from the nuclear symbol.

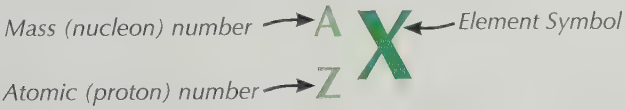


Figure 3: *Nuclear symbol.*

Tip: You can find the symbol and atomic number for each element using the periodic table. The other number in the periodic table isn't the mass number though — it's the relative atomic mass, which is a bit different. (See page 45 for more on relative atomic mass.)

Mass (nucleon) number

This is the total number of protons and neutrons in the nucleus of an atom.

Atomic (proton) number

This is the number of protons in the nucleus of an atom — it identifies the element. All atoms of the same element have the same number of protons. Sometimes the atomic number is left out of the nuclear symbol, e.g. ^{7}Li. You don't really need it because the element's symbol tells you its value.

Atoms and ions

For neutral atoms, which have no overall charge, the number of electrons is the same as the number of protons. The number of neutrons is just mass number minus atomic number, i.e. 'top minus bottom' in the nuclear symbol. Figure 4 shows some examples.

Nuclear symbol	Atomic number	Mass number	Protons	Electrons	Neutrons
$^{7}_{3}\text{Li}$	3	7	3	3	7 – 3 = 4
$^{19}_{9}\text{F}$	9	19	9	9	19 – 9 = 10
$^{24}_{12}\text{Mg}$	12	24	12	12	24 – 12 = 12

Figure 4: *Calculating the number of neutrons in atoms.*

Tip: Ions have the same number of protons and neutrons as atoms do — it's only the number of electrons that changes.

Ions have different numbers of protons and electrons. Negative ions have more electrons than protons and positive ions have fewer electrons than protons. It kind of makes sense if you think about it.

Examples

F^- is a negative ion.

The negative charge means that there's 1 more electron than there are protons. F has 9 protons (see table above), so F^- must have 10 electrons. The overall charge = + 9 – 10 = –1.

Mg^{2+} is a positive ion.

The 2+ charge means that there are 2 fewer electrons than there are protons. Mg has 12 protons (see table above), so Mg^{2+} must have 10 electrons. The overall charge = +12 – 10 = +2.

Tip: Ions are easy to spot — they've always got a $^+$ or a $^-$ next to them. If they've got a $^+$ it means they've lost electrons. If it's a $^-$ then they've gained electrons. If there's a number next to the sign it means more than one electron has been lost or gained. For example, $^{3+}$ means 3 electrons have been lost, $^{2-}$ means that 2 have been gained.

Isotopes

Isotopes of an element are atoms with the same number of protons but different numbers of neutrons.

Examples

Chlorine-35 and chlorine-37 are examples of isotopes. They have different mass numbers, which means they have different numbers of neutrons. The atomic numbers are the same. Both isotopes have 17 protons and 17 electrons.

Chlorine-35: $^{35}_{17}\text{Cl}$ **Chlorine-37:** $^{37}_{17}\text{Cl}$

35 – 17 = 18 neutrons 37 – 17 = 20 neutrons

Here's another example — naturally occurring magnesium consists of 3 isotopes.

^{24}Mg (79%)	^{25}Mg (10%)	^{26}Mg (11%)
12 protons	12 protons	12 protons
12 neutrons	13 neutrons	14 neutrons
12 electrons	12 electrons	12 electrons

Figure 5: *Subatomic particles in Mg isotopes.*

Tip: You can show isotopes in different ways. For example, the isotope of magnesium with 12 neutrons can be shown as:

Magnesium-24,

^{24}Mg or $^{24}_{12}\text{Mg}$

It's the number and arrangement of electrons that decides the chemical properties of an element. Isotopes have the same configuration of electrons, so they've got the same chemical properties. Isotopes of an element do have slightly different physical properties though, such as different densities, rates of diffusion, etc. This is because physical properties tend to depend more on the mass of the atom.

Practice Questions — Application

Q1 Aluminium has the nuclear symbol: ${}^{27}_{13}\mathrm{Al}$

a) How many protons does an atom of aluminium have?
b) How many electrons does an atom of aluminium have?
c) How many neutrons does an atom of aluminium have?

Q2 A specific potassium atom has 19 electrons and 20 neutrons.
a) How many protons does this potassium ion have?
b) What is the mass number of this potassium atom?
c) Write the nuclear symbol for potassium.
d) Potassium ions have a charge of 1+. How many electrons does a potassium ion have?

Q3 An isotope of calcium has the nuclear symbol: ${}^{40}_{20}\mathrm{Ca}$
It forms Ca^{2+} ions.
a) How many electrons does a Ca^{2+} ion have?
b) How many neutrons does a Ca^{2+} ion have?

Q4 Element A has 41 protons and 52 neutrons.
a) Write the nuclear symbol for element A.
b) Another isotope of element A has 53 neutrons. Write the nuclear symbol for this isotope of element A.

Q5 This question relates to the atoms or ions A to D:

A ${}^{16}_{8}\mathrm{O}^{2-}$ B ${}^{17}_{7}\mathrm{N}$ C ${}^{20}_{10}\mathrm{Ne}$ D ${}^{18}_{8}\mathrm{O}$

Identify the similarity for each of the following pairs.
a) A and C.
b) A and D.
c) B and C.
d) B and D.
e) Which two of the atoms or ions are isotopes of each other? Explain your reasoning.

Exam Tip
In your exam you'll have to look at the periodic table to find the nuclear symbol of an element. You usually won't be given it in the question like this.

Tip: Here we mean similarities in the numbers of protons, neutrons or electrons between the two atoms or ions.

Practice Questions — Fact Recall

Q1 Name the three types of particle found in an atom.
Q2 Give the relative masses of these particles.
Q3 State where in the atom each of these particles would be found.
Q4 What is mass number?
Q5 What is atomic number?
Q6 How can you work out the number of neutrons an atom has?
Q7 What are isotopes?
Q8 Why do isotopes have the same chemical properties?
Q9 Explain why isotopes can have different physical properties.

Learning Objectives:

- Know how different models for atomic structure can be used to explain different phenomena, e.g. the Bohr model explains periodic properties.
- Know how the models of atomic structure have changed over time and how evidence is used to accept or reject particular models.

Specification Reference 2.1.1

2. Atomic Models

The model of the atom is useful for understanding loads of ideas in chemistry. But it's just a model, and the accepted model of the atom has changed throughout history.

HOW SCIENCE WORKS

Changes to the atomic model

The Bohr model of the atom (the one on page 43) is the model of the atom you need to know for your exam — it's also one of the currently accepted models. It fits all the observations and evidence we have so far, so we assume it's true until someone shows that it's incomplete or wrong. In the past, completely different models were accepted, because they fitted the evidence available at the time.

Some ancient Greeks thought that all matter was made from indivisible particles. At the start of the 19th century John Dalton described atoms as solid spheres, and said that different types of sphere made up the different elements (see Figure 1).

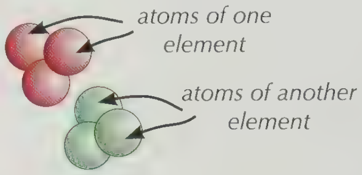


Figure 1: *Dalton's model of the atom.*

But as scientists did more experiments, our currently accepted models began to emerge, with modifications or refinements being made to take account of new evidence.

Tip: This topic is all about how science works — scientists come up with a theory which fits the current experimental evidence and that theory changes as more experimental evidence is collected.

Thomson's model

In 1897 J J Thomson did a whole series of experiments and concluded that atoms weren't solid and indivisible. His measurements of charge and mass showed that an atom must contain even smaller, negatively charged particles. He called these particles 'corpuscles' — we call them electrons. The 'solid sphere' idea of atomic structure had to be changed. The new model was known as the '**plum pudding model**' — a positively charged sphere with negative electrons embedded in it.

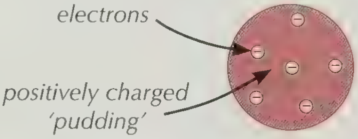


Figure 2: *Thomson's model of the atom.*

Figure 3: *Thomson and Rutherford worked together at Cambridge University.*

Rutherford's model

In 1909 Ernest Rutherford and his students Hans Geiger and Ernest Marsden conducted the famous gold foil experiment. They fired alpha particles (which are positively charged) at an extremely thin sheet of gold. From the plum pudding model, they were expecting most of the alpha particles to be deflected very slightly by the positive 'pudding' that made up most of an atom. In fact, most of the alpha particles passed straight through the gold atoms, and a very small number were deflected backwards through more than 90°. This showed that the plum pudding model couldn't be right. So Rutherford came up with a model that could explain this new evidence — the **nuclear model of the atom**. In this model, there's a tiny, positively charged nucleus at the centre of the atom surrounded by a 'cloud' of negative electrons. Most of the atom's mass is concentrated at the centre and so most of the atom is empty space (see Figure 4).

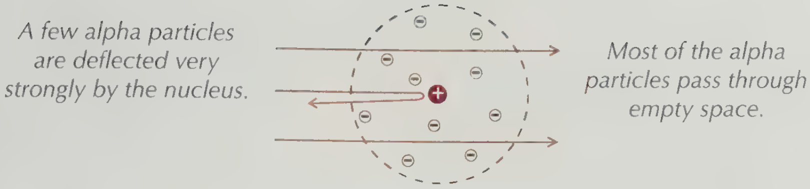

A few alpha particles are deflected very strongly by the nucleus.
Most of the alpha particles pass through empty space.

Figure 4: *Rutherford's model of the atom.*

Tip: This model is closer to the currently accepted model of an atom but still isn't quite right. Read on to find out why...

Modifications to Rutherford's model

Rutherford's model seemed pretty convincing, but Henry Moseley discovered that the charge of the nucleus increased from one element to another in units of one. This led Rutherford to investigate the nucleus further. He finally discovered that it contained positively charged particles that he called protons. The charges of the nuclei of different atoms could then be explained — the atoms of different elements have a different number of protons in their nucleus. There was still one problem with the model — the nuclei of atoms were heavier than they would be if they just contained protons. Rutherford predicted that there were other particles in the nucleus, that had mass but no charge — and the neutron was eventually discovered by James Chadwick.

This is nearly always the way scientific knowledge develops — new evidence prompts people to come up with new, improved ideas. Then other people go through each new, improved idea with a fine-tooth comb as well — modern '**peer review**' is part of this process.

Tip: See page 39 for more on protons and neutrons.

Tip: See page 2 for more on 'peer review'.

Bohr's model

The **Bohr model** (Figure 6) was a further improvement. Scientists realised that electrons in a 'cloud' around the nucleus of an atom, as Rutherford described, would quickly spiral down into the nucleus, causing the atom to collapse. Niels Bohr proposed a new model of the atom with four basic principles:

- Electrons only exist in fixed orbits (shells) and not anywhere in between.
- Each shell has a fixed energy.
- When an electron moves between shells electromagnetic radiation is emitted or absorbed.
- Because the energy of shells is fixed, the radiation will have a fixed frequency.

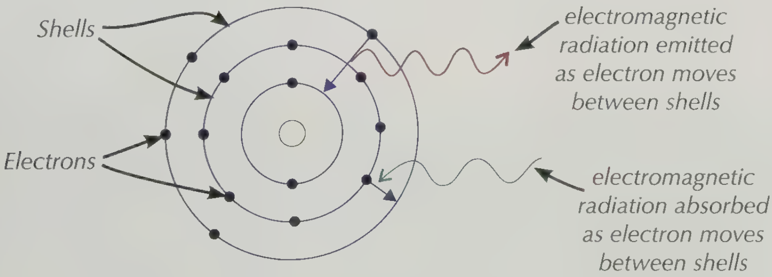

Shells
Electrons
electromagnetic radiation emitted as electron moves between shells
electromagnetic radiation absorbed as electron moves between shells

Figure 6: *Bohr's model of the atom.*

Figure 5: *Rutherford and Bohr worked together at the University of Manchester.*

The frequencies of radiation emitted and absorbed by atoms were already known from experiments. The Bohr model fitted these observations.

The Bohr model also explained why some elements (the noble gases) are inert. Bohr said that the shells of an atom can only hold fixed numbers of electrons, and that an element's reactivity is due to its electrons. So, when an atom has full shells of electrons it's stable and does not react.

Tip: The term inert just means that it doesn't react with anything.

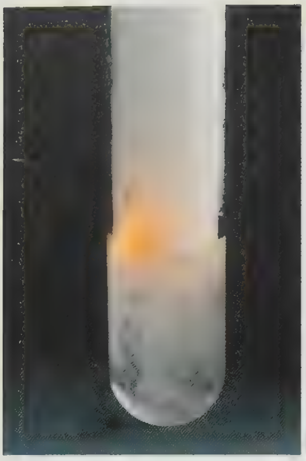


Figure 9: *Sodium reacts vigorously with water as it is very reactive.*

Examples

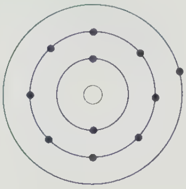


Figure 7: *Atomic structure of sodium (Bohr model).*

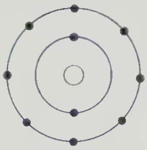


Figure 8: *Atomic structure of neon (Bohr model).*

Sodium only has 1 electron in its outer shell. This shell isn't full, so sodium is unstable and will react.

Neon (a noble gas) has full shells of electrons. This means the atom is stable, so neon will not react.

Other atomic models

We now know that the Bohr model is not perfect — but it's still widely used to describe atoms because it is simple and explains many observations from experiments, like bonding and ionisation energy trends. The most accurate model we have today involves complicated quantum mechanics — see Figure 10. Basically, you can never know where an electron is or which direction it's going in at any moment, but you can say how likely it is to be at a certain point in the atom. Oh, and electrons can act as waves as well as particles. But you don't need to worry about that.

Tip: Science is constantly progressing as evidence is found to support or disprove current theories. Some of the atomic models we believe to be accurate today may become outdated in years to come as new evidence is found to disprove them.

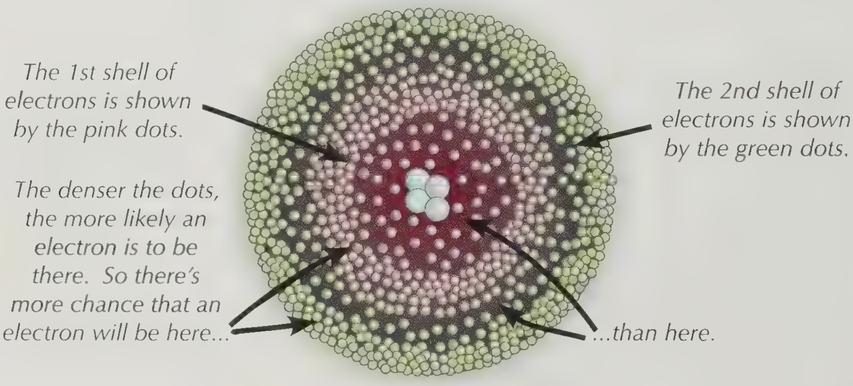

The 1st shell of electrons is shown by the pink dots.
The denser the dots, the more likely an electron is to be there. So there's more chance that an electron will be here...
The 2nd shell of electrons is shown by the green dots.
...than here.

Figure 10: *The quantum model of an atom.*

The **quantum model** might be more accurate, but it's a lot harder to get your head round and visualise. It does explain some observations that can't be accounted for by the Bohr model though. So scientists use whichever model is most relevant to whatever they're investigating.

Practice Questions — Fact Recall

Q1 Describe how J J Thomson's model of the atom was different from Dalton's model.

Q2 What name was given to J J Thomson's model of the atom?

Q3 Name the scientists who conducted the gold foil experiment in 1909.

Q4 Explain how the gold foil experiment provided evidence that Thomson's model was wrong.

Q5 Describe Rutherford's model of the atom.

Q6 Describe the main features of Bohr's model of the atom.

Q7 Is the Bohr model a true representation of the structure of the atom?

3. Relative Mass

The actual mass of an atom is very, very tiny. Don't worry about exactly how tiny for now, but it's far too small to weigh using your average pair of scales. So, the mass of one atom is compared to the mass of carbon–12. This is its relative mass. You need to know about relative atomic mass, relative isotopic mass, relative molecular mass and relative formula mass. Phew... let's get cracking...

Relative atomic mass

The **relative atomic mass**, A_r, is the weighted mean mass of an atom of an element, compared to 1/12 of the mass of an atom of carbon-12. The relative atomic mass of each element is shown in the periodic table (see Figure 1). Relative atomic mass is an average, so it's not usually a whole number.

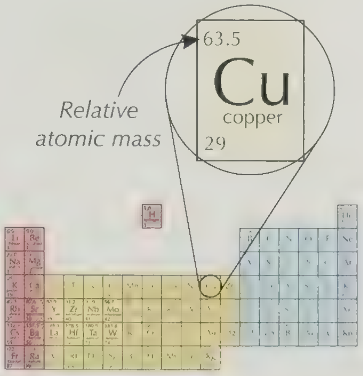


Figure 1: *Location of relative atomic masses on the periodic table.*

Relative isotopic mass

Relative isotopic mass is the mass of an atom of an isotope of an element compared to 1/12 of the mass of an atom of carbon-12. At this level, you'll find the relative isotopic mass is usually rounded to a whole number.

Calculating relative atomic mass

You need to know how to calculate the relative atomic mass (A_r) of an element from its isotopic abundances. Different isotopes of an element occur in different quantities, or **isotopic abundances**. The relative atomic mass (A_r) of an element is the average mass of all its isotopes. If you've got the isotopic abundances as percentages, the easiest way to calculate the relative atomic mass is to imagine you have 100 atoms, and then find the average mass. Just follow these steps:

- Multiply each relative isotopic mass by its % relative isotopic abundance and add up the results.
- Divide by 100.

Example — Maths Skills

Calculating the A_r of boron.

The relative atomic mass of boron is the average mass of all boron atoms. 20.0% of the boron atoms found on Earth have a relative isotopic mass of 10.0, while 80.0% have a relative isotopic mass of 11.0. To calculate the relative atomic mass, just follow the steps above:

- Multiply each relative isotopic mass by its % relative isotopic abundance and add up the results:

  $(10.0 \times 20.0) + (80.0 \times 11.0) = 200 + 880 = 1080$
- Divide this by 100: $1080 \div 100 = 10.8$

So the relative atomic mass of boron is 10.8.

Learning Objectives:

- Be able to define the terms relative isotopic mass and relative atomic mass, based on the mass of an atom of carbon-12.
- Be able to use mass spectra to determine the relative isotopic masses and relative abundances of isotopes.
- Be able to use mass spectra to calculate the relative atomic mass of an element from the relative abundances of its isotopes.
- Be able to use the terms relative molecular mass, M_r, and relative formula mass and calculate their values from relative atomic masses.

Specification Reference 2.1.1

Exam Tip
You could be asked for the definition of relative atomic mass and relative isotopic mass. These are easy marks to get in the exam if you make the effort to learn them now.

Tip: The process of finding an average explains why the relative atomic mass is not usually a whole number.

Figure 2: A scientist using a mass spectrometer to analyse a sample in a research lab.

Tip: On mass spectra like this one you can treat the mass/charge ratio as the isotopic mass because the charge is usually just +1.

Relative atomic mass and mass spectra

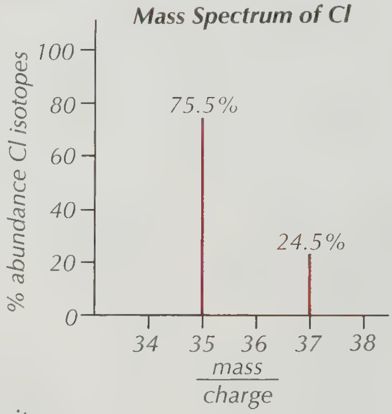
You might be given your isotopic abundances in the form of a graph, such as a **mass spectrum**. Mass spectra are produced by mass spectrometers — devices which are used to find out what samples are made up of by measuring the masses of their components (see pages 272-275).

- The y-axis gives the abundance of ions, often as a percentage. For an element, the height of each peak gives the relative isotopic abundance.
- The x-axis units are given as a 'mass/charge' ratio.

Example — Maths Skills

Calculating the relative atomic mass of chlorine.

The graph on the right shows the mass spectrum of chlorine. As with the example on the last page, the abundances are given as percentages. The peak on the left tells you 75.5% of the chlorine atoms are chlorine-35 atoms, and the peak on the right tells you 24.5% of the atoms are chlorine-37 atoms.



Once you've read the isotopic masses and their relative abundances off the spectrum, you can just follow the same method as before.

- Multiply each relative isotopic mass by its % isotopic abundance and add up the results:
  (35 × 75.5) + (37 × 24.5) = 2642.5 + 906.5 = 3549
- Divide this by 100: 3549 ÷ 100 = 35.5 (1 d.p.)

So the relative atomic mass of chlorine is 35.5.

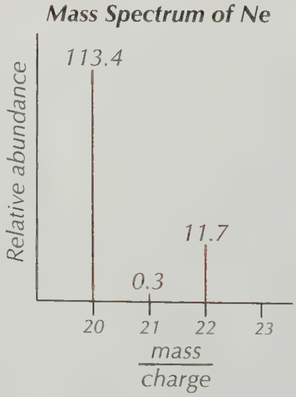
In some cases, the isotopic abundances on a mass spectrum might not be given as percentages, but as a relative abundance. The method for working out the A_r is very similar:

- Multiply each relative isotopic mass by its relative abundance and add up the results.
- Then divide by the sum of the relative abundances.

Example — Maths Skills

Calculating the relative atomic mass of neon.

The graph on the right shows the mass spectrum for a sample of neon gas. You can use this mass spectrum to calculate the A_r of neon.



- Multiply each relative isotopic mass by its relative isotopic abundance, and add up the results: (20 × 113.4) + (21 × 0.3) + (22 × 11.7) = 2531.7
- Divide by the sum of the relative abundances:
  Sum of relative abundances =
  113.4 + 0.3 + 11.7 = 125.4
  2531.7 ÷ 125.4 = 20.2 (to 1 d.p.)

So the relative atomic mass of neon is 20.2.

Exam Tip
When calculating the relative atomic mass of an element, it's always worth checking your answer against a periodic table. Under normal conditions, your answer should be the same as, or similar to, the mass (nucleon) number of that element.

Relative molecular mass

The **relative molecular mass**, M_r, is the average mass of a molecule compared to 1/12 of the mass of an atom of carbon-12.
To find the M_r, just add up the relative atomic mass values of all the atoms in the molecule.

Examples — **Maths Skills**

Calculating the relative molecular mass of C_2H_6O.
In one molecule of C_2H_6O there are 2 atoms of carbon, 6 of hydrogen and 1 of oxygen. The relative atomic masses (A_r) of each atom are shown in Figure 3.

$$M_r \text{ of } C_2H_6O = (\underset{\text{2 C atoms}}{2} \times \underset{A_r \text{ of C}}{12}) + (\overset{\text{6 H atoms}}{6} \times \overset{A_r \text{ of H}}{1}) + (\underset{\text{1 O atom}}{1} \times \underset{A_r \text{ of O}}{16}) = 46$$

Calculating the relative molecular mass of C_4H_{10}.
In one molecule of C_4H_{10} there are 4 atoms of carbon and 10 of hydrogen.

$$M_r \text{ of } C_4H_{10} = (4 \times 12) + (10 \times 1) = 58$$

Atom	A_r
Carbon (C)	12.0
Hydrogen (H)	1.0
Oxygen (O)	16.0
Calcium (Ca)	40.1
Fluorine (F)	19.0

Figure 3: *Table of relative atomic masses.*

Relative formula mass

Relative formula mass is the average mass of a formula unit, compared to 1/12 of the mass of an atom of carbon-12. It's used for compounds that are ionic (or giant covalent, such as SiO_2). To find the relative formula mass, just add up the relative atomic masses (A_r) of all the ions in the formula unit.

Exam Tip
You don't need to know the definitions of relative molecular mass and relative formula mass for your exam, but you do need to be able to calculate them and use the terms correctly.

Examples — **Maths Skills**

Calculating the relative formula mass of CaF_2.
In CaF_2 there is one Ca^{2+} ion for every two F^- ions. The A_r of ions is the same as the A_r of atoms of that element — the electrons are so small that they make no difference to the mass.

$$M_r \text{ of } CaF_2 = \overset{A_r \text{ of Ca (there's only one calcium ion)}}{40.1} + (\underset{\text{2 ions of } F^-}{2} \times \underset{A_r \text{ of F}}{19}) = 78.1$$

Calculating the relative formula mass of $CaCO_3$.
In $CaCO_3$ there is one Ca^{2+} ion for each CO_3^{2-} ion. The CO_3^{2-} ion contains 1 carbon atom and 3 oxygen atoms, so the A_r values of all these atoms need to be included in the calculation.

$$M_r \text{ of } CaCO_3 = 40.1 + 12 + (3 \times 16) = 100.1$$

Tip: Relative molecular mass and relative formula mass are basically the same thing — it's just that ionic compounds aren't made of molecules so they can't have a molecular mass. You work them out the same way though.

Practice Questions — Application

Q1 Find the relative atomic mass of the following elements:

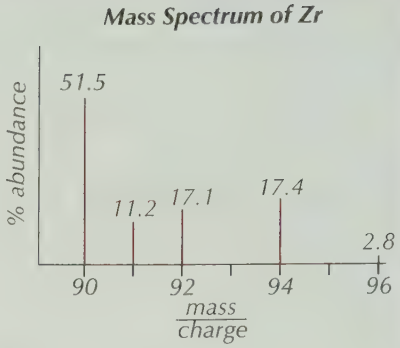
a) Rubidium

b) Mercury

c) Zinc

Q2 A sample of tungsten is 0.100% ^{180}W, 26.5% ^{182}W, 14.3% ^{183}W, 30.7% ^{184}W and 28.4% ^{186}W. Calculate the A_r of tungsten.

Q3 The mass spectrum on the right is for a sample of zirconium. Name all of the isotopes present in the sample of the element.



Tip: You might also see mass/charge as mass ÷ charge, m/z or even m : z.

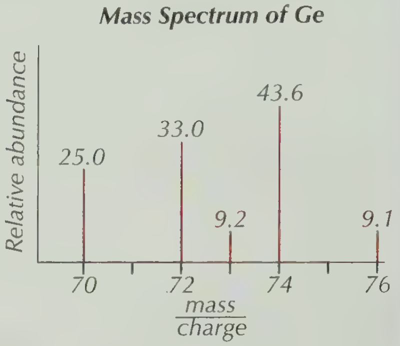
Q4 The graph on the right shows the mass spectrum of a sample of germanium. Identify the relative abundances of the following isotopes.

a) Germanium-70

b) Germanium 73

c) Germanium-76

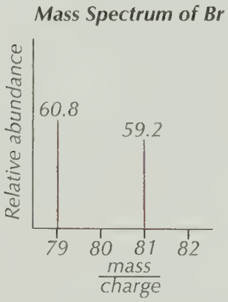
d) Germanium-74



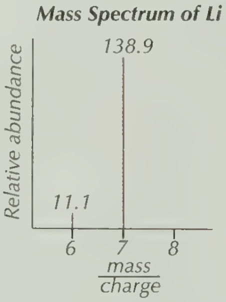
Q5 The graphs below show the mass spectra for three elements. Use the data in the graphs to calculate the relative atomic mass of each of these elements:

Tip: There's a periodic table on the last page of this book — you might need it to answer these questions.

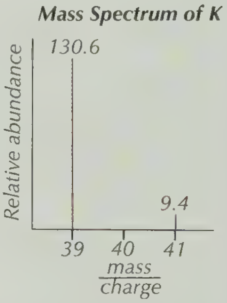
a)



b)



c)



Q6 Find the relative molecular mass of the following compounds:

a) NH_3 b) CO_2 c) $C_2H_4O_6N_2$

Q7 Find the relative formula mass of the following compounds:

a) $CaCl_2$ b) $MgSO_4$ c) NaOH

Practice Questions — Fact Recall

Q1 What is relative atomic mass?

Q2 What is relative isotopic mass?

Q3 What is relative molecular mass?

Q4 What is relative formula mass?

Exam Tip
You may be asked for the definitions in questions 1 and 2 in the exam, so now's the time to make sure you really know them.

4. The Mole

Amount of substance is a really important idea in chemistry. It's all about working out exactly how much of a chemical you have and what amount of it is reacting with other chemicals. Then you can use that information in all sorts of calculations to do with things like mass, concentration and volume.

Learning Objectives:

- Be able to explain the term amount of substance.
- Know that a mole (symbol 'mol') is the unit for amount of substance.
- Know that the Avogadro constant, N_A, is the number of particles per mole (6.02×10^{23} mol^{-1}).
- Know that molar mass (units g mol^{-1}) is the mass per mole of a substance.
- Be able to carry out calculations, using amount of substance in mol, involving mass.

Specification Reference 2.1.3

What is a mole?

Chemists often talk about 'amount of substance'. Basically, all they mean is 'number of particles'. Amount of substance is measured using a unit called the **mole** (mol for short) and given the symbol *n*. One mole is 6.02×10^{23} particles (the **Avogadro constant**, N_A). It doesn't matter what the particles are. They can be atoms, molecules, electrons, ions — anything.

Examples

In the reaction $C + O_2 \rightarrow CO_2$:

1 atom of carbon reacts with 1 molecule of oxygen to make 1 molecule of carbon dioxide, so 1 mole of carbon reacts with 1 mole of oxygen molecules to make 1 mole of carbon dioxide.

In the reaction $2Mg + O_2 \rightarrow 2MgO$:

2 atoms of magnesium react with 1 molecule of oxygen to make 2 molecules of magnesium oxide, so 2 moles of magnesium react with 1 mole of oxygen molecules to make 2 moles of magnesium oxide.

Here's a nice simple formula for finding the number of moles from the number of atoms or molecules:

$$\text{Number of moles} = \frac{\text{Number of particles you have}}{\text{Number of particles in a mole}}$$

Exam Tip
Make sure you learn this formula — you won't be given it in the exam.

Example — **Maths Skills**

I have 1.50×10^{24} carbon atoms. How many moles of carbon is this?

$$\text{Number of moles} = \frac{1.50 \times 10^{24}}{6.02 \times 10^{23}} \approx 2.49 \text{ moles}$$

Figure 1: 1 mole of carbon.

Molar mass

Molar mass, *M*, is the mass of one mole of something. But the main thing to remember is that molar mass has the same numerical value as the relative molecular mass, M_r (or relative formula mass). The only difference is you stick a 'g mol^{-1}' for grams per mole on the end.

Examples — **Maths Skills**

Find the molar mass of $CaCO_3$.

Relative formula mass, M_r, of $CaCO_3 = 40.1 + 12 + (3 \times 16) = 100.1$

So the molar mass, *M*, is 100.1 g mol^{-1} (i.e. 1 mole of $CaCO_3$ weighs 100.1 g).

Find the molar mass of $Ni(OH)_2$.

Relative formula mass, M_r, of $Ni(OH)_2 = 58.7 + (2 \times (16 + 1)) = 92.7$

So the molar mass, *M*, is 92.7 g mol^{-1} (i.e. 1 mole of $Ni(OH)_2$ weighs 92.7 g).

Tip: Remember, to find relative formula mass, all you need to do is add up the relative atomic masses of all the atoms in the formula (see page 47).

Calculations with moles

There's a formula that connects the molar mass of a substance to the number of moles of the substance that you have. It looks like this:

$$\text{Number of moles} = \frac{\text{mass of substance}}{\text{molar mass}}$$

Exam Tip
This formula crops up in all sorts of chemistry calculations — you'll definitely need to know it by heart for your exams.

Examples — Maths Skills

How many moles of aluminium oxide are present in 5.1 g of Al_2O_3?

Molar mass of Al_2O_3 = (2 × 27.0) + (3 × 16.0) = 102 g mol^{-1}

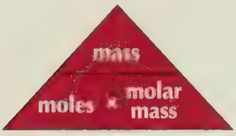
Number of moles of $Al_2O_3 = \frac{5.1}{102} = 0.05$ moles

How many moles of calcium bromide are present in 39.98 g of $CaBr_2$?

Molar mass of $CaBr_2$ = 40.1 + (2 × 79.9) = 199.9 g mol^{-1}

Number of moles of $CaBr_2 = \frac{39.98}{199.9} = 0.2$ moles

Tip: If it helps you to remember how to rearrange the equation, you could use this formula triangle:



Just cover the thing you want to calculate to find the right formula.

(For example, if you cover mass it will tell you that to calculate mass you multiply moles by molar mass.)

You can also rearrange the formula and use it to work out either the mass of a substance or its relative molecular mass:

Examples — Maths Skills

What is the mass of 2 moles of NaF?

Rearrange the formula to find mass (multiply both sides by molar mass):

$$\text{mass of substance} = \text{number of moles} \times \text{molar mass}$$

Molar mass of NaF = 23 + 19 = 42 g mol^{-1}
Mass of 2 moles of NaF = 2 × 42 = 84 g

0.050 moles of a compound weighs 2.6 g. Find its relative molecular mass.

Rearrange the formula to find molar mass:

$$\text{molar mass} = \text{mass} \div \text{number of moles}$$

Molar mass = 2.6 ÷ 0.050 = 52 g mol^{-1}. So, relative molecular mass = 52.

Multiplying the number of moles in a sample by Avogadro's constant gives you the number of molecules, particles or atoms in the sample.

Tip: In this calculation, a '...' is used to show that the number hasn't been rounded — there are extra decimal places that are used in the calculations, but aren't written down.

Example — Maths Skills

How many atoms are in 8.5 g of H_2S?

Molar mass of H_2S = 1 + 1 + 32.1 = 34.1 g mol^{-1}

Number of moles of $H_2S = \frac{8.5}{34.1} = 0.249...$ mol

To work out the number of molecules in 0.249 mol, just multiply it by Avogadro's constant:

$$\text{Number of molecules of } H_2S = 0.249... \times 6.02 \times 10^{23}$$
$$= 1.50... \times 10^{23}$$

The question asks for the number of atoms in 8.5 g of H_2S. There are 3 atoms in each molecule of H_2S (2 hydrogen atoms and 1 sulfur atom), so you need to multiply the number of molecules by 3:

$$\text{number of atoms} = 1.50... \times 10^{23} \times 3$$
$$= 4.5 \times 10^{23} \text{ atoms}$$

Exam Tip
The Avogadro constant will be given to you on your data sheet in the exam, so you don't need to worry about learning its numerical value.

Example — **Maths Skills**

How many chlorine atoms are in 71.0 g of chlorine gas ($Cl_{2\,(g)}$)?

Molar mass of $Cl_2 = 35.5 \times 2 = 71.0$ g mol^{-1}

Number of moles of $Cl_2 = \frac{71.0}{71.0} = 1.00$ mol

Number of Cl_2 molecules $= 1.00 \times 6.02 \times 10^{23}$

$= 6.02 \times 10^{23}$

There are 2 atoms in one molecule of Cl_2,

so the total number of Cl atoms $= 2 \times 6.02 \times 10^{23}$

$= 1.20 \times 10^{24}$

Figure 2: A sample of chlorine, a pale yellow gas.

Practice Questions — Application

Q1 How many atoms are in 1 mole of iron metal ($Fe_{(s)}$)?

Q2 Look at this balanced equation: $4Na + O_2 \rightarrow 2Na_2O$
How many moles of Na_2O are produced when 6 moles of Na react with 1.5 moles of O_2?

Q3 Find the molar mass of:
- a) F_2
- b) $CaCl_2$
- c) $MgSO_4$

Q4 How many moles of sodium nitrate are present in 212.5 g of $NaNO_3$?

Q5 How many moles of zinc chloride are present in 15.5 g of $ZnCl_2$?

Q6 What is the mass of 2 moles of NaCl?

Q7 What is the mass of 0.25 moles of $MgCO_3$?

Q8 1.5 moles of a mystery compound weighs 66 g. Find its molar mass.

Q9 How many O_2 molecules are in 82.1 g of oxygen gas ($O_{2\,(g)}$)?

Q10 A sample of pure magnesium sulfate, $MgSO_4$, contains 3.56×10^{24} atoms. What is the mass of the sample?

Tip: Remember — 1 mole of anything always contains the same number of particles.

Tip: You'll need to use the Avogadro constant for some of these questions. It has a value of 6.02×10^{23}.

Practice Questions — Fact Recall

Q1 a) How many particles are there in a mole?
b) What's the name for this special number?

Q2 What is the molar mass of a chemical?

Q3 What's the formula that links molar mass and number of moles?

5. Gas Volumes

Learning Objectives:

- Know that the molar gas volume (units $dm^3\ mol^{-1}$) is the gas volume per mole.
- Be able to carry out calculations, using amount of substance in mol, involving mass and gas volume.
- Know and be able to use the ideal gas equation ($pV = nRT$).
- Know the techniques and procedures required during experiments requiring the measurement of gas volumes (PAG 1).

Specification Reference 2.1.3

Calculations involving gases can be a bit complicated. The volume that a gas occupies varies, depending on conditions such as the temperature and pressure. There are some useful equations to remember, however, that will help you solve tricky, gas-related questions.

Gas Volume

If temperature and pressure stay the same, one mole of any gas always has the same volume — this is known as the molar gas volume. It has units of $dm^3\ mol^{-1}$. At room temperature and pressure (r.t.p., where temperature is 298 K and pressure is 100 kPa), the molar gas volume is $24\ dm^3\ mol^{-1}$ (or $24\ 000\ cm^3\ mol^{-1}$).

Here are two formulas for working out the number of moles in a volume of gas. Don't forget — only use them for r.t.p.

$$\text{number of moles} = \frac{\text{volume in dm}^3}{24}$$

$$\text{Or: number of moles} = \frac{\text{volume in cm}^3}{24\ 000}$$

You need to be able to use these formulas to find numbers of moles and gas volumes.

Tip: These equations only apply at room temperature and pressure. If you're asked about a gas that isn't under these conditions, you'll have to use a more sophisticated equation (see below).

Examples — **Maths Skills**

How many moles are there in $6.0\ dm^3$ of oxygen gas at r.t.p.?

Number of moles = 6.0 ÷ 24

= 0.25 moles of oxygen molecules

What volume, in cm^3, does 0.020 moles of hydrogen gas occupy at r.t.p.?

Rearrange the formula to find volume (multiply both sides by 24 000):

Volume = number of moles × 24 000

= 0.020 × 24 000 = 480 cm^3

Tip: Remember to be careful when dealing with the units. The equation you'll need to use will depend on whether you're given, or asked for, volume in cm^3 or dm^3.

The ideal gas equation

In the real world, it's not always room temperature and pressure. The **ideal gas equation** lets you find the number of moles in a certain volume at any temperature and pressure:

$$pV = nRT$$

p = pressure (Pa)

n = number of moles

T = temperature (K)

V = volume (m^3)

R = the gas constant ($J\ K^{-1}\ mol^{-1}$)

Exam Tip

The gas constant has a value of $8.314\ J\ K^{-1}\ mol^{-1}$, but this will be on the data sheet in your exam, so you don't need to worry about learning its value.

Working with the ideal gas equation is fairly straightforward — you just have to rearrange the ideal gas equation to put the unknown by itself, and substitute in the rest of the values that you're given in the question. Then it's just a matter of putting it all into your calculator to work out the answer.

Examples — Maths Skills

At what pressure would 0.400 moles of argon gas occupy 0.0100 m³ at 298 K?

Rearrange the equation to find pressure (divide both sides by V):

$$p = \frac{nRT}{V} = \frac{0.400 \times 8.314 \times 298}{0.0100} = 99\,100 \text{ Pa (3 s.f.)}$$

How many moles are there in 0.0600 m³ of hydrogen gas, at 283 K and 50 000 Pa?

Rearrange the equation to find number of moles (divide both sides by RT):

$$n = \frac{pV}{RT} = \frac{50\,000 \times 0.0600}{8.314 \times 283} = 1.28 \text{ moles (3 s.f.)}$$

Tip: Because there's more than one variable on each side of the ideal gas equation, you'll always have to rearrange it before you can use it.

If you're given the values in different units from the ones used in the ideal gas equation you'll need to convert them to the right units first.

- You might be given pressure in kPa (kilopascals). To convert from kPa to Pa you multiply by 1000 (e.g. 2 kPa = 2000 Pa).
- You might be given temperature in °C. To convert from °C to K you add 273 (e.g. 25 °C = 298 K).
- You might be given volume in cm³ or dm³. To convert from cm³ to m³ you multiply by 10^{-6}. To convert from dm³ to m³ you multiply by 10^{-3}. ($1 \text{ m}^3 = 1 \times 10^6 \text{ cm}^3 = 1 \times 10^3 \text{ dm}^3$)

Tip: All of these units are S.I. units. That means they're part of an agreed system of measurements used by scientists all over the world.

Example — Maths Skills

What volume would 2.00 moles of argon gas occupy at 27.0 °C and 100 kPa?

First put all the values you have into the right units:
$T = 27.0\ °\text{C} = (27.0 + 273)\text{ K} = 300\text{ K}$
$p = 100\text{ kPa} = 100\,000\text{ Pa}$

Now rearrange the equation to find volume (divide both sides by pressure):

$$V = \frac{nRT}{p} = \frac{2.00 \times 8.314 \times 300}{100\,000} = 0.0499 \text{ m}^3 \text{ (3 s.f.)}$$

Exam Tip
It's really easy to slip up on units — but using the wrong units will result in an incorrect answer. To prevent yourself losing marks over units in the exam, make sure you learn what units each variable of the gas equation should be in, and how to convert to them.

You might be asked to combine an ideal gas equation calculation with another type of calculation.

Example — Maths Skills

At a temperature of 60.0 °C and a pressure of 250 kPa, a gas occupied a volume of 1100 cm³ and had a mass of 1.59 g.

Find its relative molecular mass.

You've been given temperature, pressure and volume, so you need to find the number of moles:

$$n = \frac{pV}{RT} = \frac{(250 \times 10^3) \times (1.10 \times 10^{-3})}{8.314 \times 333} = 0.0993\ldots \text{ moles}$$

Now you've got the number of moles, you can calculate molar mass using the formula, molar mass = mass ÷ number of moles.

Molar mass = mass ÷ number of moles = 1.59 ÷ 0.0993... = 16.0 g mol^{-1}.

So the relative molecular mass is also 16.0.

Tip: There's a 10^3 and a 10^{-3} in this formula because the numbers have been put into standard form. There's more about standard form on pages 541-542.

Tip: This is the formula from page 50 again. Remember that molar mass has the same numerical value as relative molecular mass.

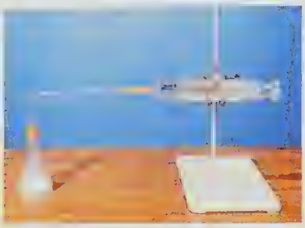


Figure 1: *An experimental set-up where gas volume is measured with a gas syringe.*

PRACTICAL ACTIVITY GROUP 1

If you ever need to measure gas volumes as part of an experiment, you should use a gas syringe (see Figure 1). The gas syringe can be attached to a reaction container to collect all the gas produced by a reaction. As the gas is produced, the plunger is pushed out of the syringe and the volume of gas collected can be read off the graduations on the side.

Care should be taken when using a gas syringe to make sure:

- the plunger can move smoothly along the syringe, without getting stuck.
- no gas can escape from the gas syringe.
- the syringe is the correct size for the experiment. If the gas syringe is too big, it may be hard to read off how much gas is produced. If it's too small, the plunger may be blown out of the end of the syringe. Not only does this mean you can't take your readings, but it could also release gas into the atmosphere. If the gas is toxic or flammable, this could be very dangerous.

Tip: It's often good practice to do experiments involving gases in a fume cupboard to prevent gases escaping into the atmosphere.

Practice Questions — Application

Q1 How many moles are there in 2.4 dm^3 of carbon dioxide gas at r.t.p.?

Q2 How many moles are in 0.65 dm^3 of carbon monoxide gas at r.t.p.?

Q3 How many moles are there in 250 cm^3 of sulfur dioxide gas at r.t.p.?

Q4 What volume, in dm^3, does 0.21 moles of hydrogen chloride gas occupy at r.t.p.?

Q5 What volume, in dm^3, does 1.1 moles of fluorine gas occupy at r.t.p.?

Q6 What volume, in cm^3, does 0.028 moles of argon gas occupy at r.t.p.?

Q7 How many moles are there in 0.04 m^3 of oxygen gas at a temperature of 350 K and a pressure of 70 000 Pa?

Q8 What volume would 0.65 moles of carbon dioxide gas occupy at a temperature of 280 K and a pressure of 100 000 Pa?

Q9 How many moles are there in 0.55 dm^3 of nitrogen gas at a temperature of 35 °C and a pressure of 90 000 Pa?

Q10 At a pressure of 110 000 Pa, 0.05 moles of hydrogen gas occupied a volume of 1200 cm^3. What was the temperature in °C?

Q11 What volume would 0.75 moles of helium gas occupy at a temperature of 22 °C and a pressure of 75 kPa?

Q12 At a temperature of 300 K and a pressure of 80 kPa a gas had a volume of 1.5 dm^3 and a mass of 2.6 g. Find its relative molecular mass.

Q13 Afiya had a sample of neon gas, Ne. They heated it to 44 °C. At this temperature the gas had a volume of 0.003 m^3. If the pressure was 100 kPa, what was the mass of the neon gas?

Practice Questions — Fact Recall

Q1 What is the formula for calculating the number of moles in a volume of gas in dm^3 at r.t.p.?

Q2 What is the formula for calculating the number of moles in a volume of gas in cm^3 at r.t.p.?

Q3 Write out the ideal gas equation. Say what the terms mean and give the standard units that each is measured in.

Q4 State why it might be dangerous to use a gas syringe that is too small, when measuring the gas produced by a reaction.

6. Concentration Calculations

The amount of substance is closely linked to the volume of a substance and its concentration. Read on to find out more...

Learning Objective:

- Be able to carry out calculations, using amount of substance in mol, involving:
  (i) mass,
  (ii) gas volume,
  (iii) solution volume and concentration.

Specification Reference 2.1.3

Moles and concentration

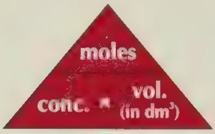
The **concentration** of a solution is how many moles (or how many grams) of something are dissolved per 1 dm^3 of solution. The units are mol dm^{-3} (or g dm^{-3}). A solution that has more moles per dm^3 than another is more concentrated. A solution that has fewer moles per dm^3 than another is more dilute. Here's the formula to find the number of moles:

$$\text{Number of moles} = \frac{\text{Concentration} \times \text{Volume (in cm}^3\text{)}}{1000}$$

$$\text{Or: Number of moles} = \text{Concentration} \times \text{Volume (in dm}^3\text{)}$$

You need to be able to use these formulas to do calculations in the exam.

Tip: This is another formula that you can stick in a formula triangle if it helps you:



Examples — Maths Skills

How many moles of lithium chloride are present in 25 cm^3 of a 1.2 mol dm^{-3} solution of LiCl?

$$\text{Number of moles} = \frac{\text{concentration} \times \text{volume (in cm}^3\text{)}}{1000}$$

$$= \frac{1.2 \times 25}{1000} = 0.030 \text{ moles}$$

Tip: 1 dm^3 is the same as 1000 cm^3 or 1 litre.

A solution of $CaCl_2$ contains 0.2 moles of calcium chloride in 0.4 dm^3 water. What is the concentration of the solution?

Rearrange the formula to find concentration (divide both sides by volume):

$$\text{concentration} = \frac{\text{number of moles}}{\text{volume (in dm}^3\text{)}}$$

$$= \frac{0.2}{0.4} = 0.5 \text{ mol dm}^{-3}$$

A 0.50 mol dm^{-3} solution of zinc sulfate contains 0.080 moles of $ZnSO_4$. What volume does the solution occupy?

Rearrange the formula to find volume (divide both sides by volume):

$$\text{volume (in dm}^3\text{)} = \frac{\text{number of moles}}{\text{concentration}}$$

$$= \frac{0.080}{0.50} = 0.16 \text{ dm}^3$$

Exam Tip
You need to know all of the formulas in this section by heart — so look out for the formula boxes, and learn them.

You might be asked to combine a concentration calculation with a molar mass calculation. This just means using two formulas, one after the other.

Example — Maths Skills

What mass of sodium hydroxide needs to be dissolved in 50 cm^3 of water to make a 2.0 mol dm^{-3} solution?

First look at the question and see what information it gives you. You've got concentration and volume — so you can work out number of moles.

Exam Tip
Remember to watch out for the units in this type of calculation. Double-check whether the volume you've been given is in cm^3 or dm^3.

Tip: Make sure all your values are in the correct units — here, the concentration is given in mol dm^{-3}, so you need to convert the volume to dm^3.

$$\text{Number of moles} = \frac{\text{concentration} \times \text{volume}\ (cm^3)}{1000}$$

$$= \frac{2.0 \times 50}{1000} = 0.10 \text{ moles of NaOH}$$

Then you can use this to work out the mass using the equation number of moles = mass ÷ molar mass

Molar mass, M, of NaOH = 23 + 16 + 1 = 40 g mol^{-1}

Mass = number of moles × M = 0.10 × 40 = 4.0 g

Tip: Chemistry is full of concentration calculations, so we've given you loads of questions to help you suss it out.

Practice Questions — Application

Q1 How many moles of potassium phosphate are present in 50 cm^3 of a 2 mol dm^{-3} solution?

Q2 How many moles of sodium chloride are present in 0.5 dm^3 of a 0.08 mol dm^{-3} solution?

Q3 How many moles of silver nitrate are present in 30 cm^3 of a 0.7 mol dm^{-3} solution?

Q4 A solution contains 0.25 moles of copper bromide in 0.5 dm^3. What is the concentration of the solution?

Q5 A solution contains 0.08 moles of lithium chloride in 0.75 dm^3. What is the concentration of the solution?

Q6 A solution contains 0.1 moles of iron oxide in 36 cm^3. What is the concentration of the solution?

Q7 A solution of calcium chloride contains 0.46 moles of $CaCl_2$. The concentration of the solution is 1.8 mol dm^{-3}. What volume does the solution occupy?

Q8 A solution of copper sulfate contains 0.01 moles of $CuSO_4$. The concentration of the solution is 0.55 mol dm^{-3}. What volume does the solution occupy?

Q9 The molecular formula of sodium oxide is Na_2O. What mass of sodium oxide would you have to dissolve in 75 cm^3 of water to make a 0.8 mol dm^{-3} solution?

Q10 The molecular formula of cobalt bromide is $CoBr_2$. What mass of cobalt bromide would you have to dissolve in 30 cm^3 of water to make a 0.5 mol dm^{-3} solution?

Q11 A solution is made by dissolving 4.08 g of a compound in 100 cm^3 of pure water. The solution has a concentration of 1.2 mol dm^{-3}. What is the molar mass of the compound?

Q12 Brine is a solution of sodium chloride, NaCl, in water. What mass of sodium chloride is dissolved in a 50 cm^3 sample of 4.1 mol dm^{-3} brine solution?

Exam Tip
Being able to convert between units is a vital skill for your exams. You'll have to be able to convert between units of mass, volume, pressure and many more...

Practice Questions — Fact Recall

Q1 What's the formula that links number of moles and concentration? (Write it out twice, once using each volume measurement.)

Q2 How many cm^3 are there in one dm^3?

Section Summary

Make sure you know...

- The structure of an atom in terms of the number of protons, neutrons and electrons.
- That the mass (nucleon) number of an atom is the total number of protons and neutrons it contains.
- That the atomic or proton number of an atom is the number of protons it contains.
- How to work out the number of protons, neutrons and electrons in atoms and ions.
- That isotopes are atoms with the same number of protons but different numbers of neutrons.
- That isotopes of an element have different masses.
- That the relative atomic mass of an element is its mass compared to 1/12 of the mass of an atom of carbon-12.
- That relative isotopic mass is the mass of an isotope of an element compared to 1/12 of the mass of an atom of carbon-12.
- How to calculate relative atomic mass from mass spectra.
- How to determine relative isotopic masses and relative abundances of isotopes from mass spectra.
- What the terms relative molecular mass and relative formula mass mean, and be able to calculate them from relative atomic masses.
- That the term amount of substance means the number of particles.
- That amount of substance is measured using a unit called the mole (mol).
- That the Avogadro constant (6.02×10^{23}) is the number of particles in one mole of a particular substance.
- That the molar mass is the mass of one mole of something and has the units g mol^{-1}.
- How to use the equation: no. of moles = mass of substance ÷ molar mass.
- How to carry out calculations using the amount of substance (in moles).
- How to calculate the volumes and number of moles of gases present at r.t.p.
- How to calculate gas volumes and related quantities, using the ideal gas equation ($pV = nRT$).
- How to carry out calculations using the amount of substance (in moles) and the volumes and concentrations of solutions.

Exam-style Questions

1 Which of these equations shows a form of the ideal gas equation?

A $pV = RT$

B $V = \frac{nRT}{p}$

C $p = \frac{nV}{RT}$

D $\frac{p}{T} = nRV$

(1 mark)

2 How many protons are in the nucleus of an atom of iodine?

A 52

B 73

C 53

D 74

(1 mark)

3 How many atoms are in a 6.30 g sample of pure nickel?

A 6.02×12^{23}

B 6.46×10^{22}

C 3.79×10^{24}

D 5.57×10^{24}

(1 mark)

4 A student is measuring the volume of gas produced by a reaction between a metal and an acid. She uses a gas syringe to collect the gas.

(a) Before starting her experiment, the student checks that there are no gaps in her apparatus. How might her readings be affected if there are gaps in the apparatus?

(1 mark)

(b) The gas produced by the experiment is highly flammable.
Suggest one safety precaution the student should take to reduce the risks associated with the production of a flammable gas.

(1 mark)

(c) To help her select appropriately sized equipment, the student works out how much gas she expects the reaction to produce before she begins the experiment.
Why might it be dangerous if the student underestimated the volume of gas produced?

(1 mark)

5 The element silicon (atomic number 14) is commonly used in electronics. There are three stable isotopes of silicon, ^{28}Si, ^{29}Si and ^{30}Si.

(a) (i) What are isotopes?

(2 marks)

(ii) Fill in the table below to show how many protons, neutrons and electrons each isotope of silicon contains.

	Protons	Neutrons	Electrons
^{28}Si			
^{29}Si			
^{30}Si			

(2 marks)

(b) The three isotopes of silicon are found naturally with the following isotopic abundances: ^{28}Si : 92.23%, ^{29}Si : 4.67% and ^{30}Si : 3.10%.

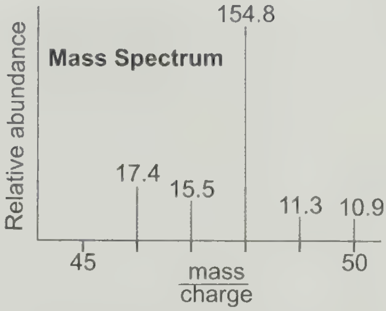
(i) Define the term relative atomic mass.

(2 marks)

(ii) Calculate the relative atomic mass of silicon. Give your answer to 2 decimal places.

(2 marks)

(c) The graph on the right shows a mass spectrum for a naturally occurring sample of an element. Determine its relative atomic mass and, therefore, suggest the identity of the element.



(2 marks)

6 At a temperature of 58.8 °C and a pressure of 178 kPa, a gas occupied a volume of 7890 cm^3 and had a mass of 22.4 g.

(a) What is the relative molecular mass of the gas?

(2 marks)

(b) A molecule of the gas is known to contain 3 atoms, two of which are oxygen. Give the name of the gas.

(2 marks)

(c) What volume would the same sample of gas occupy, in dm^3, at room temperature and pressure?

(1 mark)

Module 2 Section 2: Formulas and Equations

1. Formulas

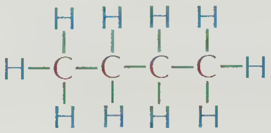
Now for a few pages about chemical formulas. A formula tells you what atoms are in a compound. Useful, I think you'll agree. There are two types you need to know about — empirical formulas and molecular formulas.

Empirical and molecular formulas

You need to know what's what with empirical and molecular formulas. The **empirical formula** gives just the smallest whole number ratio of atoms of each element in a compound. The **molecular formula** gives the actual numbers of atoms of each type of element in a molecule. The molecular formula is made up of a whole number of empirical units.

Examples

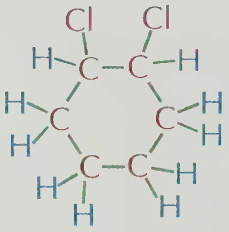
This molecule is butane:



A molecule of butane contains 4 carbon (C) atoms and 10 hydrogen (H) atoms. So its molecular formula is C_4H_{10}.

Butane's empirical formula is C_2H_5. This means that the ratio of carbon atoms to hydrogen atoms in the molecule is 2 : 5. That's as much as you can simplify it.

This molecule is 1,2-dichlorocyclohexane:



A 1,2-dichlorocyclohexane molecule contains: 6 carbon (C) atoms, 10 hydrogen (H) atoms and two chlorine (Cl) atoms.

So its molecular formula is $C_6H_{10}Cl_2$.

1,2-dichlorocyclohexane's empirical formula is C_3H_5Cl.

This means that the ratio of carbon atoms to hydrogen atoms to chlorine atoms in the molecule is 3 : 5 : 1. That's as much as you can simplify it.

If you know the empirical formula and the molecular mass of a compound, you can calculate its molecular formula. Just follow these steps:

1. Find the empirical mass (that's just the mass of the empirical formula).
2. Divide the molecular mass by the empirical mass. This tells you how many multiples of the empirical formula are in the molecular formula.
3. Multiply the empirical formula by that number to find the molecular formula.

There are a couple of examples on the next page to show you how it works.

Learning Objectives:

- Be able to use the term 'empirical formula' (the simplest whole number ratio of atoms of each element present in a compound).
- Be able to use the term 'molecular formula' (the actual number and type of atoms of each element in a molecule).

Specification Reference 2.1.3

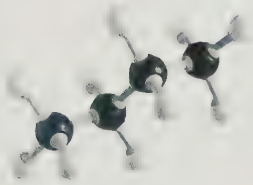


Figure 1: *Molecular model of a molecule of butane.*

Tip: There's more information coming up on pages 62-63 about how you can use experimental data to work out empirical and molecular formulas.

Tip: Empirical mass is just like relative formula mass (see page 47).

Examples — Maths Skills

A molecule has an empirical formula of $C_4H_3O_2$, and a relative molecular mass of 166. Work out its molecular formula.

1. Find the empirical mass — add up the relative atomic mass values of all the atoms in the empirical formula.

$$\text{empirical mass} = (\underset{\text{4 C atoms}}{4} \times \underset{A_r \text{ of C}}{12}) + (\overset{\text{3 H atoms}}{3} \times \overset{A_r \text{ of H}}{1}) + (\underset{\text{2 O atoms}}{2} \times \underset{A_r \text{ of O}}{16}) = 83$$

2. Divide the molecular mass by the empirical mass. The molecular mass is 166, so there are (166 ÷ 83) = 2 empirical units in the molecule.
3. The molecular formula is the empirical formula × 2, so the molecular formula = $C_8H_6O_4$.

Tip: There's more on working out molecular formulas on page 64-65.

The empirical formula of glucose is CH_2O. Its relative molecular mass is 180. Find its molecular formula.

1. Find the empirical mass of glucose.
   empirical mass = (1 × 12) + (2 × 1) + (1 × 16) = 30
2. Divide the molecular mass by the empirical mass. The molecular mass is 180, so there are (180 ÷ 30) = 6 empirical units in the molecule.
3. Molecular formula = $C_6H_{12}O_6$

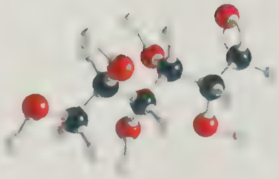


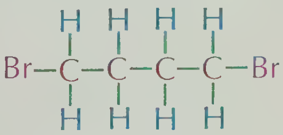
Figure 2: Molecular model of a molecule of glucose.

Practice Questions — Application

Q1 Benzene has the molecular formula C_6H_6. What is the empirical formula of benzene?

Q2 A molecule contains 2 carbon atoms, 6 hydrogen atoms and 4 oxygen atoms. Give the molecular and empirical formulas of this molecule.

Q3 The molecule below is 1,4-dibromobutane.



$$\begin{array}{ccccccccccc} & & H & & H & & H & & H & & \\ & & | & & | & & | & & | & & \\ Br & - & C & - & C & - & C & - & C & - & Br \\ & & | & & | & & | & & | & & \\ & & H & & H & & H & & H & & \end{array}$$

a) What is the molecular formula of 1,2-dibromobutane?

b) What is the empirical formula of 1,2-dibromobutane?

Q4 A molecule has the empirical formula C_4H_9, and a relative molecular mass of 114. Find its molecular formula.

Q5 A molecule has the empirical formula $C_3H_5O_2$, and a relative molecular mass of 146. Find its molecular formula.

Q6 A molecule has the empirical formula $C_4H_6Cl_2O$, and a relative molecular mass of 423. Find its molecular formula.

Practice Questions — Fact Recall

Q1 What does the empirical formula of a compound tell you?

Q2 What does the molecular formula of a compound tell you?

Learning Objective:

- Be able to calculate empirical and molecular formulas, from composition by mass or percentage composition by mass and relative molecular mass.

Specification Reference 2.1.3

2. Calculating Formulas

You can work formulas out using experimental data or percentage compositions. You need to know how to calculate both empirical and molecular formulas, so here's how.

Calculating empirical formulas

There are two different ways of calculating empirical formulas you need to know about — calculating them from experimental data and calculating them from percentage compositions.

Calculating empirical formulas from experimental data

You need to be able to work out empirical formulas from the masses of the products created in a reaction. To do this, just follow these steps:

1. Use the equation moles = mass ÷ M_r to work out how many moles of each product has been made.
2. Use the moles of each product made to work out how many moles of each atom you started with.
3. You can then write down the ratio of moles present at the start.
4. Divide by the smallest number of moles to get a whole number ratio.
5. This tells you the empirical formula.

Exam Tip
Make sure you write down all your working for calculation questions. You'll be more likely to spot any mistakes and if you do go wrong you might get some marks for the working.

Example — Maths Skills

When a hydrocarbon is burnt in excess oxygen, 4.4 g of carbon dioxide and 1.8 g of water are made. What is the empirical formula of the hydrocarbon?

1. The moles of CO_2 and H_2O produced are:

$$\text{moles } CO_2 = \frac{\text{mass}}{M_r} = \frac{4.4}{12 + (16 \times 2)} = \frac{4.4}{44} = 0.10 \text{ moles}$$

$$\text{moles } H_2O = \frac{\text{mass}}{M_r} = \frac{1.8}{(2 \times 1) + 16} = \frac{1.8}{18} = 0.10 \text{ moles}$$

2. 1 mole of CO_2 contains 1 mole of carbon atoms, so you must have started with 0.10 moles of carbon atoms.

   1 mole of H_2O contains 2 moles of hydrogen atoms, so you must have started with 0.20 moles (0.1 × 2) of hydrogen atoms.
3. If you started with 0.10 moles of C and 0.20 moles of H the C : H ratio is 0.10 : 0.20.
4. Dividing both sides by 0.10 (the smallest number of moles) gives a whole number C : H ratio of 1 : 2.
5. So the empirical formula of this hydrocarbon is CH_2.

Tip: A hydrocarbon is something that only contains hydrogen and carbon.

Tip: This method works because the only place the carbon in the carbon dioxide and the hydrogen in the water could have come from is the hydrocarbon.

Sometimes there might only be one product and you'll be told the mass of one of the reactants used instead. If this happens you can calculate the mass of the other reactant used with this equation:

mass of reactant A = mass of product – mass of reactant B

Once you know the mass of both reactants you can work out the moles of each reactant used and from there you can use points 4 and 5 above to find the empirical formula.

Tip: This equation is just the rearranged version of:

mass of products = mass of reactants

Example — Maths Skills

2.4 g of magnesium ribbon burns in air to produce a white powder which has a mass of 4.0 g. What is the empirical formula of the white powder?

If 2.4 g of magnesium has burnt to give 4.0 g of magnesium oxide then $4.0 - 2.4 = 1.6$ g of oxygen must be added. So, moles of Mg and O_2 used are:

$$\text{moles Mg} = \frac{\text{mass}}{M_r} = \frac{2.4}{24.3} = 0.10 \text{ moles}$$

$$\text{moles O} = \frac{\text{mass}}{M_r} = \frac{1.6}{16} = 0.10 \text{ moles}$$

So the ratio of Mg to O is 0.10 : 0.10. Dividing both sides by 0.10 gives a whole number ratio of 1 : 1, so the empirical formula of magnesium oxide must be MgO.

***Figure 1:** Magnesium ribbon burning in air.*

Practice Questions — Application

Q1 When a hydrocarbon is burnt in excess oxygen, 17.6 g of carbon dioxide and 10.8 g of water are made. What is the empirical formula of the hydrocarbon?

Q2 When a hydrocarbon is burnt in excess oxygen, 3.52 g of carbon dioxide and 2.88 g of water are made. What is the empirical formula of the hydrocarbon?

Q3 5.52 g of sodium burns in air to produce 7.44 g of sodium oxide. What is the empirical formula of sodium oxide?

Q4 50.2 g of iron reacts with air to produce 69.4 g of an iron oxide. What is the empirical formula of this iron oxide?

Tip: If something is in excess, it means there's much more of it than anything else. This means it doesn't limit the reaction.

Calculating empirical formulas from percentage compositions

You need to know how to work out empirical formulas from the percentages of the different elements. Follow these steps each time:

1. Assume you've got 100 g of the compound — you can turn the percentages straight into masses. Then you can work out how many moles of each element are in 100 g of the compound.
2. Divide each number of moles by the smallest number of moles you found in step 1. This gives you the ratio of the elements in the compound.
3. Apply the numbers from the ratio to the formula.

Tip: Percentage compositions tell you what percentage of the mass of a molecule is made up of each element. So if a molecule contains 26% carbon by mass, 26% of the mass of that molecule is made up of carbon atoms.

Example — Maths Skills

A compound is found to have percentage composition 56.5% potassium, 8.70% carbon and 34.8% oxygen by mass. Calculate its empirical formula.

1. If you had 100 g of the compound you would have 56.5 g of potassium, 8.70 g of carbon and 34.8 g of oxygen. Use the formula, moles = mass ÷ M_r, to work out how many moles of each element that is.

$$\text{K: } \frac{56.5}{39.1} = 1.445 \text{ moles} \quad \text{C: } \frac{8.70}{12} = 0.725 \text{ moles} \quad \text{O: } \frac{34.8}{16} = 2.175 \text{ moles}$$

2. Divide each number of moles by the smallest number (0.725 here).

$$\text{K: } \frac{1.445}{0.725} = 2.0 \quad \text{C: } \frac{0.725}{0.725} = 1.0 \quad \text{O: } \frac{2.175}{0.725} = 3.0$$

This tells you that the ratio of K : C : O in the molecule is 2 : 1 : 3.

3. So you know the empirical formula's got to be K_2CO_3.

Tip: You should add up the percentages each time there's a question like this to make sure they add up to 100% and you haven't missed out any elements.

Sometimes you might only be given the percentage of some of the elements in the compound. Then you'll have to work out the percentages of the others.

Example — Maths Skills

An oxide of nitrogen contains 26% by mass of nitrogen. Calculate its empirical formula.

1. The compound only contains nitrogen and oxygen, so if it is 26% N it must be 100 – 26 = 74% O. So if you had 100 g of the compound you would have 26 g of nitrogen and 74 g of oxygen.

   $$\text{N: } \frac{26}{14} = 1.86 \text{ moles} \qquad \text{O: } \frac{74}{16} = 4.63 \text{ moles}$$

2. Divide each number of moles by 1.86.

   $$\text{N: } \frac{1.86}{1.86} = 1.0 \qquad \text{O: } \frac{4.63}{1.86} = 2.5$$

   This tells you that the ratio of N : O in the molecule is 1 : 2.5.

3. All the numbers in an empirical formula have to be whole numbers, so you need to multiply the ratio by 2 to put it into its simplest whole number form: 2 × (1 : 2.5) = 2 : 5. So the empirical formula is N_2O_5.

Tip: If you don't know one of the percentages, just take the percentages that you do know away from 100 to find it.

Practice Questions — Application

Q1 A compound is found to have percentage composition 5.9% hydrogen and 94.1% oxygen by mass. Find its empirical formula.

Q2 A compound is found to have percentage composition 20.2% aluminium and 79.8% chlorine by mass. Find its empirical formula.

Q3 A compound is found to have percentage composition 8.50% carbon, 1.40% hydrogen and 90.1% iodine by mass. Find its empirical formula.

Q4 A compound containing only vanadium and chlorine is found to be 32.3% vanadium by mass. Find its empirical formula.

Q5 An oxide of chromium contains 31.58% by mass of oxygen. Find its empirical formula.

Tip: Being able to calculate empirical formulas is an important skill in chemistry. It's really useful when analysing the structures of compounds and might crop up in exam questions for later modules, so make sure you understand it.

Calculating molecular formulas

Once you know the empirical formula, you just need the molar mass and you can work out the molecular formula too. Dividing the molar mass by the mass of the empirical formula tells you what factor you need to scale the empirical formula up by to get the molecular formula.

Example — Maths Skills

When 4.6 g of an alcohol, with molar mass 92 g mol^{-1}, is burnt in excess oxygen, it produces 8.8 g of carbon dioxide and 5.4 g of water. Calculate the empirical formula for the alcohol and then its molecular formula.

First, find the empirical formula using the same steps as before:

$$\text{moles } CO_2 = \frac{\text{mass}}{M_r} = \frac{8.8}{12 + (16 \times 2)} = \frac{8.8}{44} = 0.20 \text{ moles}$$

1 mole of CO_2 contains 1 mole of carbon atoms, so you must have started with 0.20 moles of carbon atoms.

Tip: Alcohols contain carbon, hydrogen and oxygen.

Tip: See page 47 for more on finding relative molecular mass.

$$\text{moles } H_2O = \frac{\text{mass}}{M_r} = \frac{5.4}{(2 \times 1) + 16} = \frac{5.4}{18} = 0.30 \text{ moles}$$

1 mole of H_2O contains 2 moles of hydrogen atoms (H), so you must have started with (0.30 × 2) = 0.60 moles of hydrogen atoms.

To find the moles of oxygen coming from the alcohol you first need to find the mass of oxygen you started with. You can find this by using the moles of C and H that you calculated above to find the mass of C and H you started with and then take this away from the total mass of the alcohol:

Mass of C = no. of moles × M_r = 0.20 × 12 = 2.4 g

Mass of H = no. of moles × M_r = 0.60 × 1 = 0.60 g

Mass of alcohol = mass of C + mass of H + mass of O, so...

Mass of O = 4.6 – (2.4 + 0.60) = 1.6 g

$$\text{moles O in the alcohol} = \frac{\text{mass}}{M_r} = \frac{1.6}{16} = 0.10 \text{ moles}$$

You know the ratio — C : H : O = 0.20 : 0.60 : 0.10 = 2 : 6 : 1
So the empirical formula is C_2H_6O.

The mass of the empirical formula is (12 × 2) + (1 × 6) + 16 = 46 g

Divide the molar mass of the alcohol by this and you get 92 ÷ 46 = 2

So you need to scale the empirical formula up by 2 to get the molecular formula. So the molecular formula of the alcohol is $C_4H_{12}O_2$.

Tip: You need to work out the mass of oxygen in this way because you don't know how much oxygen has come from the alcohol itself and how much has come from the air when the alcohol was burnt.

Figure 2: An alcohol burning in air.

Practice Questions — Application

Q1 3.1 g of phosphorus burns in air to produce 7.1 g of phosphorus oxide which has a molar mass of 284 g mol^{-1}. Calculate the empirical formula of phosphorus oxide and then its molecular formula.

Q2 A hydrocarbon is found to have a percentage composition of 85.7% carbon and 14.3% hydrogen by mass. Find the molecular formula of this hydrocarbon given that it has a molar mass of 56 g mol^{-1}.

Q3 An oxide of chlorine has a molar mass of 167 g mol^{-1} and contains 42.5% chlorine by mass. Find its molecular formula.

Q4 When 12.8 g of an alcohol, with molar mass 32 g mol^{-1}, is burnt in excess oxygen, it produces 17.6 g of CO_2 and 14.4 g of H_2O. Calculate the empirical and molecular formulas of the alcohol.

Q5 When 2.64 g of an alcohol, with a molar mass 88 g mol^{-1}, is burnt in excess oxygen, it produces 2.16 g of H_2O and 5.28 g of CO_2. Calculate the empirical and molecular formulas of the alcohol.

Practice Questions — Fact Recall

Q1 What equation links the number of moles of a substance to its mass and molecular formula?

Q2 What is meant by the percentage composition of a compound?

Tip: If the molar mass of the empirical formula is the same as the molar mass of your substance then the empirical formula is the same as the molecular formula.

3. Chemical Equations

Learning Objective:

- Be able to construct balanced chemical equations (including ionic equations) for reactions studied and for unfamiliar reactions given appropriate information.

Specification Reference 2.1.2

Balancing equations is one of those topics that gets everywhere in chemistry. You'll have done this before, so it should look a bit familiar. Make sure you've got your head round it now though, because you'll definitely need it again.

How to balance equations

Balanced equations have the same number of each atom on both sides. They're.. well... you know... balanced. You can only add more atoms by adding whole reactants or products. You do this by putting a number in front of a substance or changing one that's already there. You can't mess with formulas — ever (e.g. you can change H_2O to $2H_2O$, but never to H_4O).

Examples — Maths Skills

Balance the equation $H_2SO_4 + NaOH \rightarrow Na_2SO_4 + H_2O$.

First you need to count how many of each atom you have on each side.

$$H_2SO_4 + NaOH \rightarrow Na_2SO_4 + H_2O$$

H = 3 Na = 1 | H = 2 Na = 2
O = 5 S = 1 | O = 5 S = 1

The left side needs 2 Na's, so try changing NaOH to 2NaOH:

$$H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + H_2O$$

H = 4 Na = 2 | H = 2 Na = 2
O = 6 S = 1 | O = 5 S = 1

Now the right side needs 4 H's, so try changing H_2O to $2H_2O$:

$$H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$$

H = 4 Na = 2 | H = 4 Na = 2
O = 6 S = 1 | O = 6 S = 1

Both sides have the same number of each atom — the equation is balanced.

Balance the equation $C_2H_6 + O_2 \rightarrow CO_2 + H_2O$.

First work out how many of each atom you have on each side.

$$C_2H_6 + O_2 \rightarrow CO_2 + H_2O$$

C = 2 H = 6 | C = 1 H = 2
O = 2 | O = 3

The right side needs 2 C's, so try $2CO_2$. It also needs 6 H's, so try $3H_2O$.

$$C_2H_6 + O_2 \rightarrow 2CO_2 + 3H_2O$$

C = 2 H = 6 | C = 2 H = 6
O = 2 | O = 7

The left side needs 7 O's, so try $3\frac{1}{2}O_2$ (you can use ½ to balance equations).

$$C_2H_6 + 3\frac{1}{2}O_2 \rightarrow 2CO_2 + 3H_2O$$

C = 2 H = 6 | C = 2 H = 6
O = 7 | O = 7

This balances the equation.

Exam Tip
Being able to balance equations is an extremely important skill in Chemistry. Whenever you write an equation in an exam it should be balanced, whether the question specifically asks you to balance it or not.

Tip: You can only really use ½ to balance equations containing diatomic molecules like O_2, H_2 or Cl_2. You couldn't have $\frac{1}{2}H_2O$ for example because that would involve splitting an oxygen atom.

Tip: Always do a quick check to make sure your final equation balances.

Ionic equations

You can write **ionic equations** for any reaction involving ions that happens in solution. In ionic equations, only the reacting particles are included, so you don't have to worry about the rest of the stuff. First, you make sure that both sides of the equation have the same number of atoms — just like a normal equation. Then you just take out anything that appears on both sides.

Examples — Maths Skills

Work out the ionic equation for the reaction between sodium hydroxide and nitric acid: $HNO_3 + NaOH \rightarrow NaNO_3 + H_2O$

First, you check the full equation is balanced. This one is — there are the same numbers of each type of atom on each side of the equation.

The ionic substances in this equation will dissolve, breaking up into ions in solution. You can now rewrite the equation to show all the ions that are in the reaction mixture:

$$H^+ + NO_3^- + Na^+ + OH^- \rightarrow Na^+ + NO_3^- + H_2O$$

To get from this to the ionic equation, just cross out any ions that appear on both sides of the equation — in this case, that's the sodium ions and the nitrate ions.

$$H^+ + \cancel{NO_3^-} + \cancel{Na^+} + OH^- \rightarrow \cancel{Na^+} + \cancel{NO_3^-} + H_2O$$

So the ionic equation is: **$H^+ + OH^- \rightarrow H_2O$**

Once you've written an ionic equation, check that the charges are balanced. In this example, the net charge on the left-hand side is +1 + (–1) = 0, and the net charge on the right-hand side is 0 — so the charges balance.

Work out the ionic equation for this reaction:

$$Na_3PO_{4\,(aq)} + CaCl_{2\,(aq)} \rightarrow NaCl_{(aq)} + Ca_3(PO_4)_{2\,(s)}$$

First, balance the equation so there are the same number of atoms on each side. Look back at the last page for more on how to do this.

$$2Na_3PO_4 + 3CaCl_2 \rightarrow 6NaCl + Ca_3(PO_4)_2$$

Now split up everything that dissolves into its constituent ions. Remember to take into account the reaction stoichiometry (see page 68) and the number of atoms of each type in the equation.

$$(2 \times 3)Na^+ + 2PO_4^{3-} + 3Ca^{2+} + (3 \times 2)Cl^- \rightarrow 6Na^+ + 6Cl^- + Ca_3(PO_4)_2$$

And cross out the bits that are on both sides of the equation.

$$\cancel{6Na^+} + 2PO_4^{3-} + 3Ca^{2+} + \cancel{6Cl^-} \rightarrow \cancel{6Na^+} + \cancel{6Cl^-} + Ca_3(PO_4)_2$$

This leaves you with your ionic equation: **$2PO_4^{3-} + 3Ca^{2+} \rightarrow Ca_3(PO_4)_2$**

Practice Questions — Application

Q1 Balance these equations:

a) $Mg + HCl \rightarrow MgCl_2 + H_2$

b) $S_8 + F_2 \rightarrow SF_6$

c) $Ca(OH)_2 + H_2SO_4 \rightarrow CaSO_4 + H_2O$

d) $Na_2CO_3 + HCl \rightarrow NaCl + CO_2 + H_2O$

e) $C_4H_{10} + O_2 \rightarrow CO_2 + H_2O$

Q2 Write out the ionic equations for these reactions:

a) $Fe_{(s)} + CuSO_{4\,(aq)} \rightarrow FeSO_{4(aq)} + Cu_{(s)}$

b) $BaCl_{2\,(aq)} + Na_2SO_{4(aq)} \rightarrow NaCl_{(aq)} + BaSO_{4\,(s)}$

c) $Na_2CO_{3\,(aq)} + HNO_{3\,(aq)} \rightarrow NaNO_{3\,(aq)} + H_2O_{(l)} + CO_{2\,(g)}$

Tip: Leave anything that isn't an ion in solution, like water, as it is.

Tip: As long as you use a full, balanced equation to make your ionic equation, the charges in your ionic equation should balance.

Tip: The equation shows $Ca_3(PO_4)_2$ is a solid, so you don't need to split it up into its ions.

Tip: Make sure you've got the same number of atoms on each side of the equation after each step. It's easy to lose or gain some along the way, especially if your molar ratios aren't 1 : 1 (see next page).

Tip: The net charge on the left-hand side is (2 × –3) + (3 × +2) = 0. This is the same as the net charge on the right-hand side, so your equation balances.

Tip: If you're not sure what the charges on the ions of different elements are, or how to work them out, look at pages 71-72.

4. Equations and Calculations

Once you've made sure that an equation is balanced, you can use it to calculate all sorts of things — like how much product a reaction will make...

Learning Objectives:

- Be able to use stoichiometric relationships in calculations.
- Be able to carry out calculations, using amount of substance in mol, involving mass and gas volume.
- Be able to use state symbols.

Specification Reference 2.1.2, 2.1.3

Calculating masses

Balanced equations (see page 66) show the reaction stoichiometry. The reaction stoichiometry tells you the ratios of reactants to products, i.e. how many moles of product are formed from a certain number of moles of reactants. You can use the balanced equation for a reaction to work out how much product you will get from a certain mass of reactant. Here's how:

1. Write out the balanced equation for the reaction.
2. Work out how many moles of the reactant you have.
3. Use the **molar ratio** from the balanced equation to work out the number of moles of product that will be formed from this much reactant.
4. Calculate the mass of that many moles of product.

Tip: The big numbers in front of substances in the chemical equation show the molar ratio — this is the ratio of the moles of each reactant and product in a balanced chemical equation.

Example — Maths Skills

Calculate the mass of iron(III) oxide produced if 28 g of iron is burnt in air.

1. Write out the balanced equation: $2Fe_{(s)} + 1\frac{1}{2}O_{2\,(g)} \rightarrow Fe_2O_{3\,(s)}$
2. Work out how many moles of iron you have:
   M_r of Fe = 55.8
   Moles = mass ÷ M_r = 28 ÷ 55.8 = 0.5 moles of iron
3. The molar ratio of Fe : Fe_2O_3 is 2 : 1. This means that for every 2 moles of Fe that you have, you will produce 1 mole of Fe_2O_3.
   But you only have 0.5 moles of Fe here.
   So you will produce: 0.5 ÷ 2 = 0.25 moles of Fe_2O_3.
4. Now find the mass of 0.25 moles of Fe_2O_3:
   M_r of Fe_2O_3 = (2 × 55.8) + (3 × 16) = 159.6
   Mass = moles × M_r = 0.25 × 159.6 = 40 g of iron(III) oxide

You can use similar steps to work out how much of a reactant you had at the start of a reaction when you're given a certain mass of product:

Tip: Reactants are the chemicals you start with that get used up during a reaction. Products are the chemicals that are formed during a reaction.

Example — Maths Skills

Hydrogen gas can react with nitrogen gas to give ammonia (NH_3). Calculate the mass of hydrogen needed to produce 6.8 g of ammonia.

1. $N_{2\,(g)} + 3H_{2\,(g)} \rightarrow 2NH_{3\,(g)}$
2. M_r of NH_3 = 14 + (3 × 1) = 17
   Moles = mass ÷ M_r = 6.8 ÷ 17 = 0.40 moles of NH_3
3. From the equation: the molar ratio of NH_3 : H_2 is 2 : 3.
   So to make 0.40 moles of NH_3, you must need to start with (0.40 ÷ 2) × 3 = 0.60 moles of H_2
4. M_r of H_2 = 2 × 1 = 2
   Mass = moles × M_r = 0.60 × 2 = 1.2 g of hydrogen

Tip: Ammonia is produced from nitrogen and hydrogen by the Haber process. There's more about this on pages 182 and 183.

Practice Questions — Application

Q1 3.30 g of zinc is dissolved in hydrochloric acid, producing zinc chloride ($ZnCl_2$) and hydrogen gas.

a) Write a balanced equation for this reaction.

b) Calculate the number of moles of zinc in 3.30 g.

c) How many moles of zinc chloride does the reaction produce?

d) What mass of zinc chloride does the reaction produce?

Q2 Saanvi burns some ethene gas (C_2H_4) in oxygen, producing carbon dioxide gas and 15.0 g of water.

a) Write a balanced equation for this reaction.

b) Calculate the number of moles of water in 15.0 g.

c) How many moles of ethene did the student begin with?

d) What mass of ethene did the student begin with?

Q3 Calculate the mass of barium carbonate ($BaCO_3$) produced if 4.58 g of barium chloride ($BaCl_2$) is reacted with sodium carbonate (Na_2CO_3).

Figure 1: *Zinc dissolving in hydrochloric acid.*

Calculating gas volumes

It's pretty handy to be able to work out how much gas a reaction will produce, so that you can use large enough apparatus. Or else there might be a rather large bang. The first three steps of this method are the same as the method on the last page. Once you've found the number of moles of product, the final step is to put that number into one of the gas equations that you saw on page 52.

Examples — **Maths Skills**

What volume of hydrogen gas is produced when 15 g of sodium is reacted with excess water at r.t.p.?

1. $2Na_{(s)} + 2H_2O_{(l)} \rightarrow 2NaOH_{(aq)} + H_{2(g)}$
2. M_r of Na = 23
   number of moles = mass ÷ M_r
   = 15 ÷ 23 = 0.652... moles of sodium
3. From the equation: the molar ratio of Na : H_2 is 2 : 1.
   So 0.65 moles of Na must produce (0.652... ÷ 2) = 0.326... moles of H_2

At room temperature and pressure 1 mole of gas takes up 24 dm^3.
Volume in dm^3 = number of moles × 24
= 0.326... × 24 = 7.8 dm^3 of hydrogen gas

What volume of carbon dioxide is produced when 10 g of calcium carbonate reacts with excess hydrochloric acid at r.t.p.?

1. $CaCO_{3(s)} + 2HCl_{(aq)} \rightarrow CaCl_{2(aq)} + CO_{2(g)} + H_2O_{(l)}$
2. M_r of $CaCO_3$ = 40.1 + 12 + (3 × 16) = 100.1
   number of moles = mass ÷ M_r
   = 10 ÷ 100.1 = 0.10 moles of calcium carbonate
3. From the equation: the molar ratio of $CaCO_3$: CO_2 is 1 : 1.
   So 0.10 moles of $CaCO_3$ must produce 0.10 moles of CO_2.

At room temperature and pressure 1 mole of gas takes up 24 dm^3.
Volume in dm^3 = number of moles × 24
= 0.10 × 24 = 2.4 dm^3 of carbon dioxide

Tip: 'Excess water' just means that all of the sodium will react.

Tip: In these calculations you need to use the molar ratios which you get from the balanced equation. See the last page for more on molar ratios.

State symbols

State symbols are put after each substance in an equation. They tell you what state of matter things are in:

s = solid, l = liquid, g = gas, aq = aqueous (solution in water).

Example

$$CaCO_{3\ (s)} + 2HCl_{\ (aq)} \rightarrow CaCl_{2\ (aq)} + H_2O_{\ (l)} + CO_{2\ (g)}$$

solid *aqueous* *aqueous* *liquid* *gas*

Practice Questions — Application

Q1 Give the state symbols that you would use in an equation to show the state of the following substances.

a) a solution of magnesium chloride in water

b) a piece of magnesium metal

c) a measured amount of water (at r.t.p.)

d) a solution of sodium nitrate in water

e) ethane gas

f) copper oxide powder

Q2 9.0 g of water is split apart to produce hydrogen gas and oxygen gas.

a) Write a balanced equation for this reaction.

b) Calculate the number of moles of water in 9.0 g.

c) How many moles of oxygen gas does the reaction produce?

d) What volume of oxygen gas will the reaction produce at r.t.p.?

Q3 7.00 g of zinc sulfide (ZnS) is burnt in oxygen. This produces solid zinc oxide (ZnO) and sulfur dioxide gas (SO_2).

a) Write a balanced equation for this reaction.

b) Calculate the number of moles of zinc sulfide in 7.00 g.

c) How many moles of sulfur dioxide gas does the reaction produce?

d) What volume of sulfur dioxide gas will the reaction produce at r.t.p.?

Q4 A sample of hexane gas (C_6H_{14}) is cracked to give butane gas (C_4H_{10}) and ethene gas (C_2H_4). The mass of butane produced is 3.00 g.

a) Write a balanced equation for this reaction.

b) Calculate the number of moles of butane in 3.00 g.

c) How many moles of hexane gas were present in the sample?

d) What volume would this many moles of hexane gas occupy at r.t.p.?

Q5 Magnesium metal, once ignited, will react with oxygen in the air to produce solid magnesium oxide. Calculate the volume of oxygen, at r.t.p., needed to create 10 g of MgO.

Exam Tip

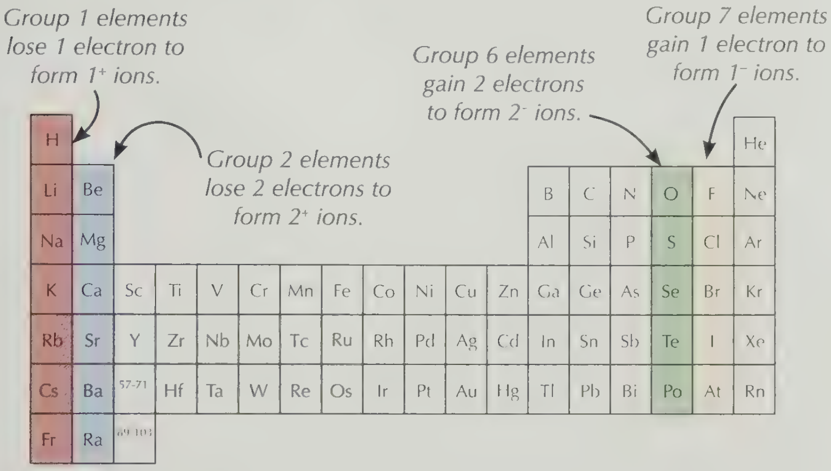
Make sure any chemical equations you write are balanced. You'll find you use balanced equations in loads of calculations and it's really important you know the right amounts of products compared to reactants.

5. Formulas of Ionic Compounds

The periodic table is a useful tool for predicting how different elements will behave. This includes working out what ions each element is likely to form.

Formation of ions

Ions are formed when electrons are transferred from one atom to another. The simplest ions are single atoms which have either lost or gained electrons so as to have a full outer shell. You don't have to remember what ion each element forms — nope, for many of them you just look at the periodic table. Elements in the same group all have the same number of outer electrons. So they have to lose or gain the same number to get the full outer shell that they're aiming for. And this means that they form ions with the same charges.



Group 1 elements lose 1 electron to form 1⁺ ions.
Group 2 elements lose 2 electrons to form 2⁺ ions.
Group 6 elements gain 2 electrons to form 2⁻ ions.
Group 7 elements gain 1 electron to form 1⁻ ions.
H He
Li Be B C N O F Ne
Na Mg Al Si P S Cl Ar
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Cs Ba 57-71 Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po At Rn
Fr Ra 89-103

Figure 1: *The ions formed by elements in the groups of the periodic table.*

Example

What charged ion is sulfur likely to form?

First you need to identify which group sulfur is in by looking at a copy of the periodic table.

Sulfur is in Group 6. Elements in Group 6 gain two electrons to form ions with a –2 charge. So, the sulfur will form a 2– ion (S^{2-}).

Not all ions are made from single atoms. There are many ions that are made up of a group of atoms with an overall charge. These are called molecular ions. You'll need to learn the names and formulas of the ones in Figure 2.

Name	Formula
Nitrate	NO_3^-
Carbonate	CO_3^{2-}
Sulfate	SO_4^{2-}
Hydroxide	OH^-
Ammonium	NH_4^+

Figure 2: *The names and formulas of common molecular ions.*

Learning Objectives:

- Be able to write the formulas of ionic compounds from ionic charges.
- Be able to predict the ionic charge from the position of an element in the periodic table.
- Know the names and formulas of the following ions: NO_3^-, CO_3^{2-}, SO_4^{2-}, OH^-, NH_4^+, Zn^{2+}, Ag^+.

Specification Reference 2.1.2

Tip: You can write half-equations to show the formation of ions. For example:

$Na \rightarrow Na^+ + e^-$

$O + 2e^- \rightarrow O^{2-}$

Tip: Metals tend to form ions with a charge that's the same as their group number. Non-metals form ions with a charge that's equal to their group number minus eight.

Exam Tip

You'll need to remember the charges on some other common ions. You need to know that zinc forms 2+ ions (Zn^{2+}) and that silver forms 1+ ions (Ag^+).

The formulas of ionic compounds

1. **Ionic compounds** are made when positive and negative ions bond together. They do this through **ionic bonding** (see pages 110-112).
2. The charges on an ionic compound must always balance out to zero. For example:

- In NaCl, the +1 charge on the Na^+ ion balances the –1 charge on the Cl^- ion.
- In $MgCl_2$, the +2 charge on the Mg^{2+} ion balances the two –1 charges on the two Cl^- ions.

Figure 3: Crystals of magnesium chloride, $MgCl_2$.

To work out the formula of an ionic compound, you just have to work out the ratio between the positive and negative ions so that the total of all the negative charges is the same as the total of the positive charges.

Examples

What is the formula of potassium sulfate?

Potassium is in Group 1 of the periodic table, so will form ions with a +1 charge: K^+.

The formula for the sulfate ion is SO_4^{2-}.

For every one sulfate ion, you will need two potassium ions to balance the charge: $(+1 \times 2) + (-2) = 0$.

So the formula is K_2SO_4.

What is the formula of silver nitrate?

The charge on a silver ion is +1 — the formula of the silver ion is Ag^+ (this is unfortunately just a charge you have to learn — you can't work it out from silver's position in the periodic table).

The formula for the nitrate ion is NO_3^-.

Each silver ion exactly balances each nitrate ion, so they exist in a 1 : 1 ratio: $+1 + (-1) = 0$.

So the formula is $AgNO_3$.

Exam Tip
You'll be given a periodic table in your exam, so you don't need to remember which group all the elements are in.

Practice Questions — Application

Q1 Use the periodic table to give the charge on the following ions:
a) hydrogen b) lithium c) iodine

Q2 An ionic compound is formed when calcium and chlorine react together. Give the formula of the compound formed.

Q3 Zinc nitrate is an ionic compound.
a) What is the charge on a zinc ion?
b) What is the formula of a nitrate ion?
c) Give the formula of zinc nitrate.

Tip: The periodic table on the last page of this book should help you with these questions.

Tip: When you're asked for the formula of an ion, remember to include the charge, as well as the chemical formula.

Practice Questions — Fact Recall

Q1 What charge do the ions formed by Group 1 elements have?

Q2 Which elements does the carbonate ion contain?

Q3 What is the charge on a silver ion?

Section Summary

Make sure you know...

- That the empirical formula gives the simplest whole number ratio of atoms of each element present in a compound.
- That the molecular formula gives the actual number of atoms of each element present in a molecule.
- How to calculate empirical and molecular formulas using mass and percentage compositions.
- How to construct balanced equations for chemical reactions, including ionic equations.
- How to use balanced equations to determine stoichiometric relationships in calculations.
- How state symbols are used in chemical equations, and the meaning of the symbols (s), (l), (g) and (aq).
- How to predict the charge on an ion formed by an element, from its position in the periodic table.
- The formulas of the following ions: NO_3^-, CO_3^{2-}, SO_4^{2-}, OH^-, NH_4^+, Zn^{2+} and Ag^+.
- How to work out the formulas of ionic compounds from the charges on the ions.

Exam-style Questions

1 What is the formula of sodium nitrate?

A $NaNO_3$

B $Na(NO)_3$

C Na_2NO_3

D $NaNO_2$

(1 mark)

2 Selenium (Se) is an element in Group 6 of the periodic table.
Which ion is selenium likely to form?

A Se^-

B Se^{2-}

C Se^{6+}

D Se^{2+}

(1 mark)

3 A molecule, **X**, has the empirical formula C_3H_4O.
Which of these molecules could be molecule **X**?

A C_6H_8O

B C_2H_2O

C $C_{12}H_{14}O_3$

D $C_{15}H_{20}O_5$

(1 mark)

4 The equation below shows the reaction of magnesium carbonate ions with hydrochloric acid.

$$2HCl_{(aq)} + MgCO_{3\,(s)} \rightarrow CO_{2\,(g)} + H_2O_{(l)} + MgCl_{2\,(aq)}$$

(a) Write an ionic equation for the reaction shown above.

(2 marks)

(b) In a reaction between hydrochloric acid and magnesium carbonate at room temperature and pressure, 496.3 cm^3 of carbon dioxide gas was evolved.
What mass of magnesium carbonate must have reacted?

(4 marks)

5 Alcohols contain the elements carbon, hydrogen and oxygen.
When 9.0 g of an unknown alcohol is burnt in air, 17.6 g of CO_2 and 9.0 g of H_2O are produced.

(a) Define the term empirical formula.

(1 mark)

(b) (i) Calculate how many moles of CO_2 and H_2O are produced when this alcohol is burnt.

(2 marks)

(ii) Calculate the mass of carbon, hydrogen and oxygen present in the alcohol.

(3 marks)

(iii) Deduce the empirical formula of this alcohol.

(2 marks)

The unknown alcohol has a molar mass of 90 g mol^{-1}.

(c) (i) Define the term molecular formula.

(1 mark)

(ii) Deduce the molecular formula of this alcohol.

(2 marks)

6 Sodium hypochlorite (NaClO) is the main chemical in household bleach.
It is made in the Hooker process from chlorine molecules and sodium hydroxide.

(a) Write a balanced chemical equation for the formation of sodium hypochlorite, given that the only other products are sodium chloride and water.

(1 mark)

(b) A student attempts to synthesise a sample of bleach using the same method as that used in the Hooker process. Calculate the mass of sodium hydroxide required to make 37.1 g of sodium hypochlorite.

(3 marks)

(c) Sodium hypochlorite is an ionic compound. Given the chemical formula of sodium hypochlorite is NaClO, what is the charge on a hypochlorite ion?

(1 mark)

7 A nitrate of iron contains 59.6% by mass of oxygen.

(a) What is the formula for the nitrate ion?

(1 mark)

(b) What is the empirical formula of the nitrate of iron?

(5 marks)

1. Acids, Bases and Salts

You met acids and bases at GCSE, but you need to know even more about them now. This section is all about what acids and bases are and how they react with each other to form salts.

What are acids and bases?

Acids are proton donors.
When mixed with water, all acids release hydrogen ions — H^+.

Examples

Sulfuric acid (H_2SO_4) releases hydrogen ions when it is mixed with water:

$$H_2SO_{4(l)} + H_2O_{(l)} \rightarrow 2H^+_{(aq)} + SO_4{}^{2-}{}_{(aq)}$$

Hydrochloric acid (HCl) also releases hydrogen ions in water:

$$HCl_{(g)} + H_2O_{(l)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$$

Hydrogen atoms only contain one proton and one electron. So H^+ ions (which have lost the electron) are just protons. You never get H^+ ions by themselves in water — they're always combined with H_2O to form hydroxonium ions (H_3O^+):

$$H^+_{(aq)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)}$$

Bases do the opposite of acids
— they're proton acceptors and want to grab H^+ ions.

Examples

Ammonia (NH_3) is a base and it can accept hydrogen ions, forming ammonium ions ($NH_4{}^+$):

$$NH_{3(aq)} + H^+_{(aq)} \rightarrow NH_4{}^+{}_{(aq)}$$

OH^- ions act as bases and can accept hydrogen ions to form water:

$$OH^-_{(aq)} + H^+_{(aq)} \rightarrow H_2O_{(l)}$$

So, acids produce $H^+_{(aq)}$ ions in an aqueous solution — i.e. they're proton donors. Bases remove $H^+_{(aq)}$ ions from an aqueous solution — i.e. they're proton acceptors. Bases that are soluble in water are known as **alkalis**. They release OH^- ions in solution. You'll need to learn the names and formulas of the acids and bases in Figure 1 for your exam.

Acids	Bases
HCl (hydrochloric acid)	NaOH (sodium hydroxide)
H_2SO_4 (sulfuric acid)	KOH (potassium hydroxide)
HNO_3 (nitric acid)	NH_3 (ammonia)
CH_3COOH (ethanoic acid)	

Figure 1: *The names and formulas of some common acids and bases.*

Learning Objectives:

- Be able to explain that acids release H^+ ions in aqueous solution.
- Be able to explain that alkalis release OH^- ions in aqueous solution.
- Know the formulas of the common acids (HCl, H_2SO_4, HNO_3 and CH_3COOH).
- Know the formulas of the common alkalis (NaOH, KOH and NH_3).
- Be able to qualitatively explain strong and weak acids in terms of relative dissociations.
- Be able to describe neutralisation as the reaction of H^+ and OH^- ions to form H_2O.
- Be able to describe the neutralisation reactions of acids with bases, including carbonates, metal oxides and alkalis (water-soluble bases), to form salts, including full equations.

Specification Reference 2.1.4

Ammonia, NH_3, is a base — in fact it dissolves in water, so aqueous ammonia is an alkali. It'll happily accept a proton from an acid to form an ammonium ion — this can then form an ammonium salt.

Writing equations containing ammonium ions is a bit trickier, as ammonia doesn't directly produce hydroxide ions, but aqueous ammonia is still an alkali. This is because the reaction between ammonia and water produces hydroxide ions. As you saw on the last page, ammonia accepts a hydrogen ion from a water molecule, forming an ammonium ion and a hydroxide ion:

$$NH_{3\,(aq)} + H_2O_{(l)} \rightleftharpoons NH_4^+{}_{(aq)} + OH^-{}_{(aq)}$$

Tip: This equation is really useful as it explains really easily how ammonia acts as an alkali.

The strength of acids and bases

The reaction between an acid and water, or a base and water is reversible, so at any point in time, both the forwards and backwards reactions will be happening. So for the reaction of an acid with water:

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

Both of the following reactions are occurring:

$HA + H_2O \rightarrow H_3O^+ + A^-$ and $H_3O^+ + A^- \rightarrow HA + H_2O$

Tip: In these equations, A just represents any acid and B represents any old base.

The same applies for the reaction of a base with water:

$$B + H_2O \rightleftharpoons BH^+ + OH^-$$

In the situation above, both of the following reactions are occurring:

$B + H_2O \rightarrow BH^+ + OH^-$ and $BH^+ + OH^- \rightarrow B + H_2O$

Strong acids and bases

Acids and bases can be classed as strong or weak, depending on whether the forwards or backwards reaction is more prevalent and to what extent the acid or base is ionised in solution. For strong acids, e.g. HCl, very little of the reverse reaction happens, so nearly all the acid will dissociate (or ionise) in water, and nearly all the H^+ ions are released.

Example

Hydrochloric acid is a strong acid: $HCl_{(aq)} \rightarrow H^+{}_{(aq)} + Cl^-{}_{(aq)}$

The acid is almost 100% ionised in solution (i.e. present as H^+ and Cl^- ions, rather than as HCl), so it's a strong acid.

Tip: The reactions of strong acids and bases with water are still reversible. So little of the backwards reaction happens, however, that they're usually written as a non-reversible reaction.

The same thing applies with strong bases, e.g. NaOH. The forwards reaction is favoured, so nearly all the base dissociates in water and lots of OH^- ions are released.

Example

Sodium hydroxide is a strong base: $NaOH_{(aq)} \rightarrow Na^+{}_{(aq)} + OH^-{}_{(aq)}$

Tip: Don't get strong/weak acids confused with concentrated/dilute acids. The strength is all to do with ionisation, whereas concentration is to do with how much acid or base is dissolved in a solution.

Weak acids and bases

For weak acids, the backwards reaction is favoured, so only a small amount of the acid will dissociate in water and only a few H^+ ions are released. Reactions of weak acids are written as a reversible reaction:

Potassium hydroxide
Ammonia solution
Sodium hydroxide

Figure 2: Some common alkalis.

Example

Ethanoic acid is a weak acid: $CH_3COOH_{(aq)} \rightleftharpoons CH_3COO_{(aq)} + H^+_{(aq)}$

Again, weak bases ionise only slightly in water. The backwards reaction is favoured, so only a small amount of the base dissociates and only a few OH^- ions are released. Again, the reaction is written as a reversible reaction:

Example

Ammonia is a weak base: $NH_{3\,(aq)} + H_2O_{(l)} \rightleftharpoons NH_4{}^+_{(aq)} + OH^-_{(aq)}$

Reactions of acids and bases

Acid molecules release their hydrogen ions, so other ions can hop into their places. You get a **salt** if the hydrogen ions are replaced by metal ions or ammonium ($NH_4{}^+$) ions.

There are quite a few reactions of acids that produce salts...

Different acids produce different salts:

- Sulfuric acid (H_2SO_4) produces salts called sulfates. These contain $SO_4{}^{2-}$ (sulfate) ions — e.g. $MgSO_4$ is magnesium sulfate.
- Hydrochloric acid (HCl) produces chlorides. These contain Cl^- (chloride) ions — e.g. $MgCl_2$ is magnesium chloride.
- Nitric acid (HNO_3) produces nitrates. These contain $NO_3{}^-$ (nitrate) ions — e.g. $Mg(NO_3)_2$ is magnesium nitrate.

Tip: Acid-base reactions are known as neutralisation reactions because, if the numbers of moles of hydrogen ions and hydroxide ions are equal, the reaction results in a neutral solution.

Acid-base reactions

When acids react with bases, they neutralise each other.
The general formula for an acid-base (neutralisation) reaction is:

Acid + Base → Salt + Water

The water formed in reactions of acids and bases is formed by the hydrogen ions released by the acid, and the hydroxide ions released by the alkali. These ions combine in solution to form water molecules:

$$H^+_{(aq)} + OH^-_{(aq)} \rightleftharpoons H_2O_{(l)}$$

Example

Sodium hydroxide (NaOH) and nitric acid react to form a salt and water.

This is a reaction between an acid and a base, so the products will be a salt and water:

Acid + Base → Salt + Water

The salts produced by nitric acid are nitrates, so the salt produced by the reaction of sodium hydroxide and nitric acid will be sodium nitrate:

$$NaOH_{(aq)} + HNO_{3\,(aq)} \rightarrow NaNO_{3\,(aq)} + H_2O_{(l)}$$

The ionic equation for this reaction will be:

$$H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)}$$

Tip: Sodium is in Group 1 so forms ions with a 1+ charge. The nitrate ion has a 1– charge, so the ratio of Na to $NO_3{}^-$ ions in the sodium nitrate salt formed in this reaction is 1 : 1, and the formula is $NaNO_3$. Look back at page 72 for more on writing the formulas of ionic compounds.

Tip: See pages 66-67 for more on ionic equations.

Example

The equation of the reaction between aqueous ammonia and sulfuric acid is:

$$2NH_{3\,(aq)} + H_2O_{\,(l)} + H_2SO_{4\,(aq)} \rightarrow (NH_4)_2SO_{4\,(aq)} + H_2O_{\,(l)}$$

But because water is present on both sides of the equation, you can simplify the equation to:

$$2NH_{3\,(aq)} + H_2SO_{4\,(aq)} \rightarrow (NH_4)_2SO_{4\,(aq)}$$

The ionic equation for this reaction is:

$$NH_{3\,(aq)} + H^+_{\,(aq)} \rightarrow NH_4^+{}_{\,(aq)}$$

Tip: The reaction of ammonia and nitric acid would produce ammonium nitrate. Hydrochloric acid and ammonia would produce ammonium chloride.

Reactions of ammonia and acids produce ammonium salts. The name of the salt in the reaction above is ammonium sulfate.

Tip: The ionic equation is really useful because it applies to all reactions of ammonia with acids.

Reactions of acids with metals

Salts are also produced when acids react with metals. But this time, hydrogen is produced instead of water, so the general equation is:

Metal + Acid → Salt + Hydrogen

Example

Magnesium reacts with sulfuric acid to produce magnesium sulfate:

$$Mg_{\,(s)} + H_2SO_{4\,(aq)} \rightarrow MgSO_{4\,(aq)} + H_{2\,(g)}$$

The ionic equation for this reaction is: $Mg_{\,(s)} + 2H^+_{\,(aq)} \rightarrow Mg^{2+}_{\,(aq)} + H_{2\,(g)}$

Tip: In this reaction magnesium ions are replacing the hydrogen ions in the acid to form a salt.

Acid and metal oxide reactions

Metal oxides react with acids according to the following equation:

Metal Oxide + Acid → Salt + Water

Figure 3: Magnesium ribbon reacting with acid. The solution fizzes because hydrogen gas is produced.

Example

Magnesium oxide (MgO) reacts with hydrochloric acid to form the salt magnesium chloride ($MgCl_2$) and water. The equation for this reaction is:

$$MgO_{\,(s)} + 2HCl_{\,(aq)} \rightarrow MgCl_{2(aq)} + H_2O_{\,(l)}$$

This is the ionic equation for the reaction:

$$O^{2-}_{\,(s)} + 2H^+_{\,(aq)} \rightarrow H_2O_{\,(l)}$$

In this reaction, the O^{2-} ion accepts two H^+ ions, donated by the acid.

Acid and metal hydroxide reactions

Metal hydroxides are usually alkalis. Sodium hydroxide (NaOH) and potassium hydroxide (KOH) are the alkalis you're most likely to meet. Alkalis release OH^- ions in water. These OH^- ions accept H^+ ions (protons) from an acid to form water molecules.
The general equation for this reaction is:

Metal Hydroxide + Acid → Salt + Water

Example

Potassium hydroxide (KOH) reacts with hydrochloric acid to form the salt potassium chloride (KCl) and water. The equation for this reaction is:

$$KOH_{(aq)} + HCl_{(aq)} \rightarrow KCl_{(aq)} + H_2O_{(l)}$$

Here's the ionic equation for the reaction:

$$OH^-_{(aq)} + H^+_{(aq)} \rightarrow H_2O_{(l)}$$

The ionic equation shows that a proton is transferred from the acid to the hydroxide ion. This ionic equation is the same for all reactions between metal hydroxides and acids.

Reactions of acids with carbonates

When acids react with carbonates, a salt is produced along with water and carbon dioxide. Here's the general equation:

Metal Carbonate + Acid → Salt + Carbon Dioxide + Water

Example

Sodium carbonate reacts with hydrochloric acid to produce sodium chloride, carbon dioxide and water:

$$Na_2CO_{3\,(s)} + 2HCl_{(aq)} \rightarrow 2NaCl_{(aq)} + CO_{2\,(g)} + H_2O_{(l)}$$

The ionic equation for this reaction is: $CO_3^{2-}{}_{(s)} + 2H^+_{(aq)} \rightarrow CO_{2\,(g)} + H_2O_{(l)}$

Figure 4: *Sodium carbonate reacting with acid. It fizzes because carbon dioxide gas is produced.*

Practice Questions — Application

Q1 Write an equation to show the reaction of hydrochloric acid with:
- a) copper(II) oxide (CuO) to give copper(II) chloride ($CuCl_2$)
- b) sodium hydroxide (NaOH) to give sodium chloride (NaCl)

Q2 Write an equation to show the reaction of sulfuric acid with:
- a) iron (Fe) to give iron(III) sulfate ($Fe_2(SO_4)_3$)
- b) calcium carbonate ($CaCO_3$) to give calcium sulfate ($CaSO_4$)

Q3 Write an equation to show the reaction of nitric acid with:
- a) aluminium oxide (Al_2O_3) to give aluminium nitrate ($Al(NO_3)_3$)
- b) potassium hydroxide (KOH) to give potassium nitrate (KNO_3)
- c) magnesium carbonate ($MgCO_3$) to give magnesium nitrate ($Mg(NO_3)_2$)

Exam Tip

If you're asked to describe what you'd see when a metal reacts with an acid, you need to say that the metal disappears (dissolves) and bubbles are produced (effervescence).

Practice Questions — Fact Recall

Q1 a) What is an acid? b) What is a base?

Q2 Explain the following terms:
- a) a strong acid.
- b) a weak base.

Q3 Write down the molecular formula of:
- a) hydrochloric acid.
- b) sulfuric acid.
- c) nitric acid.
- d) sodium hydroxide.
- e) potassium hydroxide.
- f) ammonia.

Q4 What type of salt do each of the acids in Q3 form when they react?

Q5 What products are formed when an acid reacts with:
- a) a base?
- b) a metal carbonate?
- c) a metal?

Tip: If you ever have to include state symbols when writing out equations containing acids and bases, remember — generally, everything will be aqueous, apart from water which is a liquid.

2. Anhydrous and Hydrated Salts

Salts are ionic compounds, formed when acids and bases react together. They can come in two different forms — hydrated or anhydrous. Anhydrous salts don't contain water, hydrated salts do.

What are anhydrous and hydrated salts?

All solid salts consist of a **lattice** of positive and negative ions. In some salts, water molecules are incorporated in the lattice too — see Figure 1.

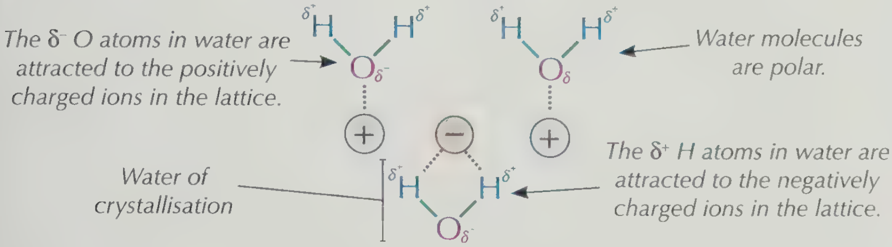

The δ⁻ O atoms in water are attracted to the positively charged ions in the lattice.
Water molecules are polar.
Water of crystallisation
The δ⁺ H atoms in water are attracted to the negatively charged ions in the lattice.
δ⁺H
Hδ⁺
Oδ⁻
+
−

Figure 1: *A small part of a lattice in a hydrated salt.*

The water in a lattice is called **water of crystallisation**. A solid salt containing water of crystallisation is **hydrated**. A salt is **anhydrous** if it doesn't contain water of crystallisation.

One mole of a particular hydrated salt always has the same number of moles of water of crystallisation — its formula shows how many (it's often a whole number, but not always...).

Example

Hydrated copper sulfate has five moles of water for every mole of the salt. So its formula is $CuSO_4.5H_2O$ (see Figures 2 and 3). There's a dot between the $CuSO_4$ and the H_2O to show that they are not joined by a covalent bond.

Finding the formulas of hydrated salts

PRACTICAL ACTIVITY GROUP 1

Many hydrated salts lose their water of crystallisation when heated, to become anhydrous. If you know the mass of the salt when hydrated and anhydrous, you can work its formula out. Just follow these steps:

- First you find the mass of water lost by taking the mass of the anhydrous salt away from the mass of the hydrated salt.
- Then you find the number of moles of water lost.
- Next find the number of moles of anhydrous salt that's produced.
- Now you work out the ratio of moles of anhydrous salt to moles of water.
- Scale up or down so that your ratio is in the form 1 : n, round off your answer and you're done.

Example

Heating 3.210 g of hydrated magnesium sulfate, $MgSO_4.XH_2O$, forms 1.567 g of anhydrous magnesium sulfate. Find the value of X and write the formula of the hydrated salt.

- The mass of water lost is 3.210 – 1.567 = 1.643 g

Learning Objectives:

- Be able to explain the terms anhydrous, hydrated and water of crystallisation.
- Be able to calculate the formula of a hydrated salt from percentage composition, mass composition or experimental data (PAG 1).

Specification Reference 2.1.3

Tip: See pages 120-127 for more on polar compounds and pages 110-112 for more on lattice structures.

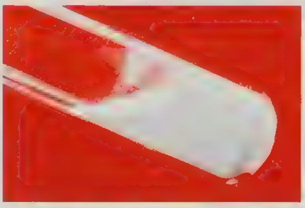


Figure 2: *Anhydrous copper sulfate ($CuSO_4$).*

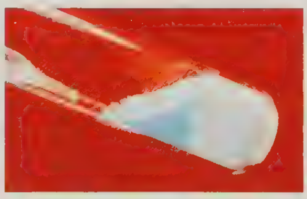


Figure 3: *When water is added, $CuSO_4.5H_2O$ forms, which is blue in colour.*

Tip: To calculate the number of moles you'll need the equation:

$$\text{moles} = \frac{\text{mass}}{\text{molar mass}}$$

See page 50 for more on this.

Tip: *M* here is the molar mass, which is the same as the molecular mass (see page 49 for a bit more explanation).

- You can now calculate the moles of water present in the hydrated salt:

$$\text{moles } H_2O = \frac{\text{mass}}{M} = \frac{1.643}{16 + (2 \times 1)} = \frac{1.643}{18} = 0.0913 \text{ moles}$$

- And you can calculate the moles of anhydrous magnesium sulfate:

$$\text{moles } MgSO_4 = \frac{1.567}{24.3 + 32.1 + (4 \times 16)} = \frac{1.567}{120.4} = 0.0130 \text{ moles}$$

- So the ratio of $MgSO_4 : H_2O = 0.0130 : 0.0913$.
- Dividing both sides by 0.0130 gives a ratio of 1 : 7.02. This shows that there are 7.02 moles of water for every one mole of $MgSO_4$.
- X must be a whole number, and some errors are to be expected in any experiment, so you can safely round off your result to 1 : 7 — so the formula of the hydrated salt is $MgSO_4.7H_2O$.

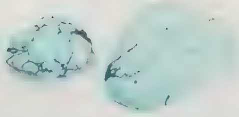


Figure 4: Some minerals are made from hydrated salts. This is turquoise, which is hydrated copper-aluminium phosphate ($CuAl_6(PO_4)_4(OH)_8.4H_2O$).

You could also be given the percentage of the mass that is water. Then, you'd work out the formula by assuming you had 100 g of the hydrated salt and converting the percentages into masses.

Tip: See pages 63-64 for more on how to work out formulas using percentage composition.

Example

Hydrated $CaCl_2$ contains 49.3% H_2O by mass. Find the formula of the hydrated salt.

- If you had 100 g of hydrated $CaCl_2$ then 49.3 g would be water and 50.7 g (100 – 49.3) would be $CaCl_2$.
- Calculating the moles gives

$$\text{moles } CaCl_2 = \frac{\text{mass}}{M} = \frac{50.7}{40.1 + (2 \times 35.5)} = \frac{50.7}{111.1} = 0.456 \text{ moles}$$

$$\text{moles } H_2O = \frac{\text{mass}}{M} = \frac{49.3}{16 + (2 \times 1)} = \frac{49.3}{18} = 2.739 \text{ moles}$$

- So the ratio of $CaCl_2 : H_2O = 0.456 : 2.739$. This is a ratio of 1 : 6, so the formula of the hydrated salt is $CaCl_2.6H_2O$.

Exam Tip

You can work out the formula of a hydrated salt from the molar mass too. All you have to do is find the molar mass of the anhydrous salt, take this away from the molar mass of the hydrated salt and divide the remaining mass by the molar mass of water to find out how many water molecules there are.

Practice Questions — Application

Q1 Heating 57.5 g of hydrated zinc sulfate ($ZnSO_4$.**X**H_2O) forms 32.3 g of anhydrous zinc sulfate. Find the value of **X** and write down the formula of the hydrated salt.

Q2 35.685 g of hydrated cobalt chloride ($CoCl_2$.**X**H_2O) contains 16.2 g of water. Find the value of **X** and write down the formula of the hydrated salt.

Q3 Hydrated $BaCl_2$ contains 14.74% H_2O by mass. Find the formula of the hydrated salt.

Q4 Hydrated $Fe(NO_3)_3$ contains 30.87% H_2O by mass. Find the formula of the hydrated salt.

Practice Questions — Fact Recall

Q1 What name is given to the water molecules in a lattice?

Q2 What does anhydrous mean?

Q3 How might a hydrated salt be converted into an anhydrous salt?

3. Titrations

You can do a titration to find the concentration of an acid or an alkali. You'll almost certainly have to do one at some point, so make sure you know how.

Performing titrations

PRACTICAL ACTIVITY GROUP 2

Titrations allow you to find out exactly how much acid is needed to neutralise a quantity of alkali. You measure out some alkali using a pipette and put it in a flask (see Figure 1), along with some indicator, e.g. phenolphthalein.

First of all, do a rough titration to get an idea where the end point is (the point where the alkali is exactly neutralised and the indicator changes colour). To do this, take an initial reading to see how much acid is in the burette to start off with. Then, add the acid to the alkali — giving the flask a regular swirl. Stop when your indicator shows a permanent colour change (the end point) (see Figure 1). Record the final reading from your burette.

Now do an accurate titration. Run the acid in to within 2 cm^3 of the end point, then add the acid dropwise. If you don't notice exactly when the solution changed colour you've overshot and your result won't be accurate. Work out the amount of acid used to neutralise the alkali. This is just the final reading minus the initial reading. This volume is known as the titre. It's best to repeat the titration a few times, making sure you get a similar answer each time — your readings should be within 0.1 cm^3 of each other. Then calculate a mean, ignoring any anomalous results.

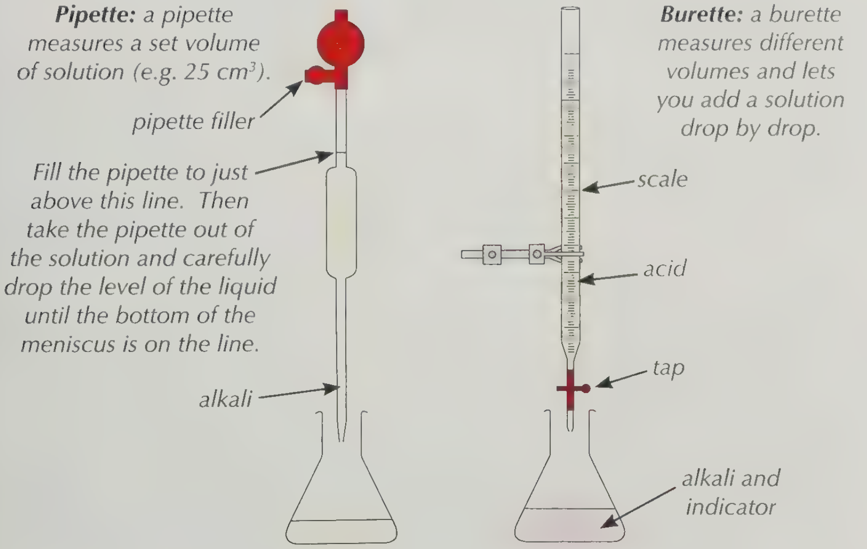

Pipette: a pipette measures a set volume of solution (e.g. 25 cm^3).
pipette filler
Fill the pipette to just above this line. Then take the pipette out of the solution and carefully drop the level of the liquid until the bottom of the meniscus is on the line.
alkali
Burette: a burette measures different volumes and lets you add a solution drop by drop.
scale
acid
tap
alkali and indicator

Figure 1: *The apparatus needed for a titration.*

Indicators

PRACTICAL ACTIVITY GROUP 2

Indicators change colour at certain pHs. In titrations, indicators that change colour quickly over a very small pH range are used so you know exactly when the reaction has ended.

There are two main indicators for acid/alkali reactions:

- methyl orange — turns from yellow to red when adding acid to alkali.
- phenolphthalein — turns from pink to colourless when adding acid to alkali.

Learning Objectives:

- Know the techniques and procedures used when preparing a standard solution of required concentration and carrying out acid-base titrations (PAG 2).
- Know the techniques and procedures required during experiments requiring the measurement of mass and volumes of solutions (PAG 1, PAG 2).
- Be able to carry out calculations, using amount of substance in mol, involving solution volume and concentration.

Specification Reference 2.1.3, 2.1.4

Tip: Remember to wash out the conical flask between each titration to remove any acid or alkali left in it.

Tip: You can also do titrations the other way round — adding alkali to acid.

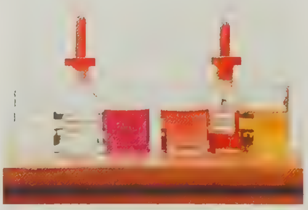


Figure 2: *The colour changes observed with phenolphthalein (left) and methyl orange (right).*

Practical techniques

Titrations are all about being precise — you need to be really careful when measuring out solids and liquids. You need to make sure that the volumes and masses you think you have are the volumes and masses you actually have.

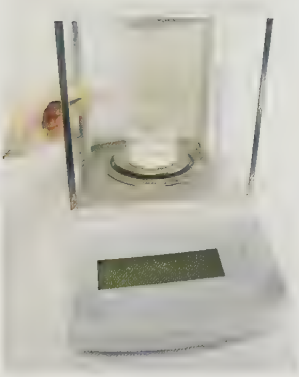


Figure 3: An analytical balance.

Measuring masses

PRACTICAL ACTIVITY GROUP 1

When you're measuring out masses, e.g. when you're making up a standard solution (see below), you should use an accurate balance that reads to a suitable number of decimal places. When weighing out solids you should:

- Reset the balance to zero before you start weighing your solid. This makes sure that the masses you record in your experiment are the actual masses of the things you're weighing.
- Make sure all of the solid you weigh is transferred from your weighing vessel to the apparatus you're using in your experiment. If you're dissolving your solid, you can do this by washing out the weighing vessel with some distilled water to make sure all the solid is transferred to the apparatus. If you're not dissolving the solid, you could compare the mass of the empty weighing vessel before and after weighing out your solid. By doing this, you can work out the mass of any traces of solid left over.

Tip: To work out how much trace solid is left in a weighing vessel, subtract the original mass of the empty weighing vessel from the mass of the vessel after the solid has been transferred from it.

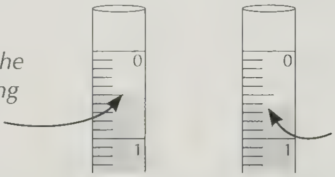
Tip: For information about precisely measuring gas volumes, look at page 54.

Measuring volumes of solutions

In titrations, burettes are a great way of measuring out liquids. When taking a reading from a burette, you should take the reading from the bottom of the meniscus. You don't have to read to the smallest graduation, e.g. 0.1 cm^3. You can make your readings more precise by taking readings to the nearest 0.05 cm^3 (see Figure 4).

PRACTICAL ACTIVITY GROUP 2

This is the bottom of the meniscus. This reading would be 0.50 cm^3.



The reading is half way between the two graduation marks. This reading would be 0.65 cm^3.

Figure 4: Volume readings using a burette.

- In titrations, you can also measure volumes using pipettes and volumetric flasks. Unlike burettes, these only measure a fixed volume, e.g. 10 cm^3, 50 cm^3, etc. For this reason, they're more suited to measuring out volumes for standard solutions or an initial volume of acid or alkali to titrate.
- When measuring volumes with pipettes and volumetric flasks, you'll need to fill the container up exactly to the graduation line. It helps to be at eye-level with the graduation line, so you can see the exact point when the bottom of the meniscus is level with the graduation line.

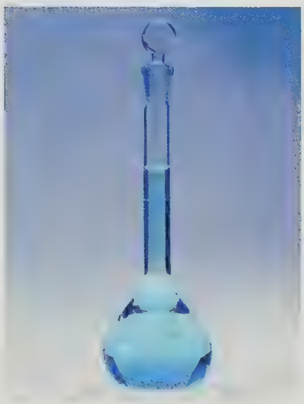


Figure 5: A volumetric flask. A mark on the neck of the flask shows where it should be filled to in order to achieve the desired volume.

Standard Solutions

In a titration, you have one unknown concentration to work out. To work out the concentration of the unknown solution, you have to know the concentration of the solution you're titrating it against.

A solution that has a precisely known concentration is called a **standard solution**. Standard solutions are made by dissolving a known amount of solid in a known amount of water to create a known concentration.

Preparing standard solutions

PRACTICAL ACTIVITY GROUP 2

To make up a standard solution, follow these steps:

1) Using a precise balance, carefully weigh out the required mass of solid onto a watch glass.
2) Transfer this solid to a beaker. Use some water to wash any bits of solid from the watch glass into the beaker.
3) Add water to the beaker to completely dissolve the solid. Use a glass rod to stir the solution to help the solid dissolve.
4) Once the solid has dissolved, transfer the solution into a volumetric flask. You'll need to use a volumetric flask that's the same size as the volume of solution you want to make up. Rinse the beaker and glass rod with water, transferring this water into the volumetric flask.
5) Use water to fill the volumetric flask up to the graduation line. Use a pipette to add the final few drops to make sure you don't add too much water and overshoot the graduation line.
6) Put the lid on the flask and turn the flask over a few times to thoroughly mix the solution.

Tip: When making standard solutions you should always use distilled water — this is just pure water that contains nothing else.

Calculations involving standard solutions

Titrations are all about concentrations (see pages 55-56). You'll need to be able to work out concentrations, as well as moles and volumes of standard solutions, using this equation:

$$\text{Number of moles} = \frac{\text{Concentration} \times \text{Volume (in cm}^3\text{)}}{1000}$$

Tip: This formula pops up all the time. It's one you need to commit to memory and know how to rearrange. If you already have the volume in dm^3, you can use the formula: number of moles = concentration × volume (in dm^3).

Examples — Maths Skills

What mass of solid sodium carbonate, Na_2CO_3, is needed to make 250 cm^3 of 0.300 mol dm^{-3} sodium carbonate solution?

Start by working out how many moles of Na_2CO_3 are needed using the equation: moles = concentration × volume

$$n = 0.300 \times \left(\frac{250}{1000}\right) = 0.0750 \text{ moles}$$

Now use the equation mass = moles × M to work out the mass of Na_2CO_3 required to make up the standard solution:

$$\text{mass} = 0.0750 \times [(2 \times 23) + 12.0 + (3 \times 16)] = 0.0750 \times 106 = 7.95 \text{ g}$$

Tip: You need to divide the concentration in cm^3 by 1000 to convert it into dm^3.

What is the concentration of a standard solution formed by dissolving 7.22 g of potassium hydroxide in 250 cm^3 water?

Start by working out how many moles of potassium hydroxide are in 7.22 g using the equation:

$$\text{Number of moles} = \frac{\text{mass of substance}}{\text{molar mass}}$$

$$n = \frac{7.22}{(39.1 + 16 + 1)} = 0.128\ldots \text{ moles}$$

Tip: This is the formula from page 50. Look back there for more information about molar mass and how to use this formula.

Now you just need to work out the concentration of the solution by substituting the number of moles and volume into this equation:

$$\text{concentration} = \frac{\text{moles}}{\text{volume}}$$

$$= \frac{0.128\ldots}{(250 \div 1000)} = 0.515 \text{ mol dm}^{-3} \text{ (3 s.f.)}$$

Once you have a standard solution of a known concentration, you can dilute it with distilled water to make further standard solutions of different concentrations using the following method:

- First divide the concentration of the standard solution you want by the concentration of the standard solution you have.
- Then multiply by the volume of new standard solution you want. This gives you the volume of the concentrated solution to use.
- Subtract this volume of concentrated solution from the total volume of dilute standard solution you desire. This gives you the amount of distilled water to use.

Tip: Once you know how much distilled water and solution you need, you can create your dilute standard solution. This is done by first measuring out the volume of concentrated standard solution you need and transferring it to a volumetric flask of the correct size. Then, fill the volumetric flask up to the graduation line with distilled water and mix.

Example — Maths Skills

How would you make 250 cm^3 of a 3.0 mol dm^{-3} standard solution from a 6.0 mol dm^{-3} standard solution?

First divide the concentration of the standard solution you want by the original concentration of the standard solution:

$$\frac{3.0}{6.0} = 0.50$$

Then multiply by the volume that you want:

$0.50 \times 250 = 125\ cm^3$

This is the volume of old standard solution you would need. In order to make 250 cm^3 of this standard solution, you would need to dilute the 125 cm^3 of 6.0 mol dm^{-3} with (250 – 125) = 125 cm^3 distilled water.

Practice Questions — Application

Q1 How many moles of NaCl are required to make 400 cm^3 of a 1.50 mol dm^{-3} solution of NaCl?

Q2 How many moles of $NaHSO_4$ are required to make 250 cm^3 of a 2.0 mol dm^{-3} standard solution?

Q3 What mass of $H_2C_2O_4$ is needed to make 500.0 cm^3 of a 1.250 mol dm^{-3} standard solution?

Q4 A student has 500 cm^3 of 1.60 mol dm^{-3} sodium hydroxide solution. They want to make 250 cm^3 of a 0.400 mol dm^{-3} solution.

a) What volume of 1.60 mol dm^{-3} sodium hydroxide solution does the student require to make the 0.400 mol dm^{-3} standard solution?

b) What volume of distilled water does the student require to make the 0.400 mol dm^{-3} standard solution?

Q5 What quantities of a stock solution of 5.00 mol dm^{-3} HCl solution and distilled water would you need to use to make 100 cm^3 of a 1.50 mol dm^{-3} HCl solution?

Figure 6: A student doing a titration. She is adding acid from the burette to the alkali in the flask. The alkali is coloured because it contains an indicator.

Practice Questions — Fact Recall

Q1 Which piece of equipment would you use to add an acid of known concentration to a conical flask of alkali, during an acid-base titration?

Q2 Name two indicators used for acid/base titrations.

Q3 What is a standard solution?

4. Titration Calculations

As if knowing how to do a titration wasn't enough, now it's time to learn how to work out concentrations from all the data you collect.

Learning Objective:

- Be able to carry out structured and non-structured titration calculations, based on experimental results of familiar and non-familiar acids and bases.

Specification Reference 2.1.4

Calculating concentration

You need to be able to use the results of a titration to calculate the concentration of acids and alkalis. There's more on concentration calculations on pages 55-56.

Examples — **Maths Skills**

25 cm³ of 0.50 mol dm⁻³ HCl neutralised 35 cm³ of NaOH solution. Calculate the concentration of the sodium hydroxide solution in mol dm⁻³.

First write a balanced equation and decide what you know and what you need to know:

$$\begin{array}{lcccc} & HCl_{(aq)} & + \; NaOH_{(aq)} & \rightarrow NaCl_{(aq)} & + \; H_2O_{(l)} \\ \textit{Volume:} & 25\ cm^3 & 35\ cm^3 & & \\ \textit{Concentration:} & 0.50\ mol\ dm^{-3} & ? & & \end{array}$$

You know the volume and concentration of the HCl, so first work out how many moles of HCl you have:

$$\text{Number of moles HCl} = \frac{\text{concentration} \times \text{volume}(cm^3)}{1000}$$

$$= \frac{0.50 \times 25}{1000} = 0.0125 \text{ moles}$$

From the equation, you know 1 mole of HCl neutralises 1 mole of NaOH.

So 0.0125 moles of HCl must neutralise 0.0125 moles of NaOH.

Now it's a doddle to work out the concentration of NaOH.

$$\text{Concentration of NaOH} = \frac{\text{moles of NaOH} \times 1000}{\text{volume}(cm^3)}$$

$$= \frac{0.0125 \times 1000}{35} = 0.36 \text{ mol dm}^{-3}$$

Exam Tip
With long wordy questions like this you might find it helpful to highlight the key bits of information in the question that you're likely to need.

Tip: The volumes in titrations are almost always in cm³ and not dm³, so you need to divide by 1000 when calculating the number of moles.

40 cm³ of 0.25 mol dm⁻³ KOH was used to neutralise 22 cm³ of HNO_3 solution. Calculate the concentration of the nitric acid in mol dm⁻³.

Write out the balanced equation and the information that you have:

$$\begin{array}{lcccc} & HNO_{3(aq)} & + \; KOH_{(aq)} & \rightarrow KNO_{3(aq)} & + \; H_2O_{(l)} \\ \textit{Volume:} & 22\ cm^3 & 40\ cm^3 & & \\ \textit{Concentration:} & ? & 0.25\ mol\ dm^{-3} & & \end{array}$$

You know the volume and concentration of the KOH, so now work out how many moles of KOH you have:

$$\text{Number of moles KOH} = \frac{\text{concentration} \times \text{volume}(cm^3)}{1000}$$

$$= \frac{0.25 \times 40}{1000} = 0.010 \text{ moles}$$

From the equation, you know 1 mole of KOH neutralises 1 mole of HNO_3.

So 0.010 moles of KOH must neutralise 0.010 moles of HNO_3.

$$\text{Concentration of } HNO_3 = \frac{\text{moles of } HNO_3 \times 1000}{\text{volume}(cm^3)}$$

$$= \frac{0.010 \times 1000}{22} = 0.45 \text{ mol dm}^{-3}$$

Tip: In this example, it's an alkali being added to an acid instead.

Exam Tip
You need to be able to work out concentration in g dm⁻³ too. To do this, just convert moles into mass and use:

$$\text{Conc} = \frac{\text{mass (g)} \times 1000}{\text{volume }(cm^3)}$$

Practice Questions — Application

Q1 28.0 cm^3 of 0.750 mol dm^{-3} hydrochloric acid (HCl) was used to neutralise 40.0 cm^3 of potassium hydroxide (KOH) solution.

a) Write a balanced equation for this reaction.

b) Calculate the number of moles of HCl used to neutralise the solution.

c) How many moles of KOH were neutralised by the HCl?

d) What was the concentration, in mol dm^{-3}, of the KOH solution?

Q2 15.3 cm^3 of 1.50 mol dm^{-3} sodium hydroxide (NaOH) was used to neutralise 35.0 cm^3 of nitric acid (HNO_3). What was the concentration, in mol dm^{-3}, of the HNO_3 solution?

Q3 12.0 cm^3 of 0.500 mol dm^{-3} HCl solution was used to neutralise 24.0 cm^3 of LiOH solution. What was the concentration, in mol dm^{-3}, of the LiOH solution?

Polyprotic acids

You may have to do calculations that involve acids that donate more than one proton. These are known as polyprotic acids.

- Diprotic acids donate two protons, e.g. sulfuric acid (H_2SO_4), carbonic acid (H_2CO_3) and hydrogen sulfide (H_2S).
- Triprotic acids donate three protons, e.g. phosphoric acid (H_3PO_4).

Compared to a monoprotic acid, you'll need double the number of moles of base to neutralise a diprotic acid. You'll need to triple the number of moles of base to neutralise a triprotic acid compared to a monoprotic acid. So, remember to take this into account when you're working out these sorts of titration calculations.

Tip: You can have polyprotic bases too, such as $Ba(OH)_2$, which is a diprotic base — it can react with 2 protons.

Tip: Polyprotic acids are sometimes called polybasic acids. Monoprotic acids can be called monobasic acids, diprotic acids can be called dibasic acids, and so on.

Calculating volumes

You can use a similar method to find the volume of acid or alkali that you need to neutralise a solution. You'll need to use the number of moles = (concentration × volume (cm^3)) ÷ 1000 formula again, but this time rearrange it to find the volume:

$$\text{volume (cm}^3\text{)} = \frac{\text{number of moles} \times 1000}{\text{concentration}}$$

Tip: All of these calculations are just like the moles, concentration and volume ones back on pages 55-56. You just apply the same method to titrations.

Example — Maths Skills

20.4 cm^3 of a 0.500 mol dm^{-3} solution of sodium carbonate reacts with 1.50 mol dm^{-3} nitric acid. Calculate the volume of nitric acid required to neutralise the sodium carbonate.

Like before, first write a balanced equation for the reaction and decide what you know and what you want to know:

	$Na_2CO_{3(aq)}$	+	$2HNO_{3(aq)}$	$\rightarrow 2NaNO_{3(aq)} + H_2O_{(l)} + CO_{2(g)}$
Volume:	*20.4 cm^3*		*?*	
Concentration:	*0.500 mol dm^{-3}*		*1.50 mol dm^{-3}*	

Now work out how many moles of Na_2CO_3 you've got:

$$\text{Number of moles } Na_2CO_3 = \frac{\text{concentration} \times \text{volume (cm}^3\text{)}}{1000}$$

$$= \frac{0.500 \times 20.4}{1000} = 0.0102 \text{ moles}$$

Tip: See page 80 for more on the reactions of acids with metal carbonates.

1 mole of Na_2CO_3 neutralises 2 moles of HNO_3, so 0.0102 moles of Na_2CO_3 neutralises (0.0102 × 2) = 0.0204 moles of HNO_3.

Now you know the number of moles of HNO_3 and the concentration, you can work out the volume:

$$\text{Volume of } HNO_3 = \frac{\text{number of moles} \times 1000}{\text{concentration}}$$

$$= \frac{0.0204 \times 1000}{1.50} = 13.6 \text{ cm}^3$$

And here's an example where you're finding the volume of alkali used.

Example — **Maths Skills**

18.2 cm³ of a 0.800 mol dm⁻³ H_2SO_4 solution reacts with 0.300 mol dm⁻³ LiOH. Calculate the volume of lithium hydroxide solution required to neutralise the sulfuric acid.

Write out the balanced equation and the information that you have:

$$H_2SO_{4(aq)} + 2LiOH_{(aq)} \rightarrow Li_2SO_{4(aq)} + 2H_2O_{(l)}$$

	$H_2SO_{4(aq)}$	$2LiOH_{(aq)}$
Volume:	*18.2 cm³*	*?*
Concentration:	*0.800 mol dm⁻³*	*0.300 mol dm⁻³*

Now work out how many moles of H_2SO_4 you've got:

$$\text{Number of moles } H_2SO_4 = \frac{\text{concentration} \times \text{volume (cm}^3)}{1000}$$

$$= \frac{0.800 \times 18.2}{1000} = 0.01456 \text{ moles}$$

1 mole of H_2SO_4 neutralises 2 moles of LiOH, so 0.01456 moles of H_2SO_4 neutralises 0.02912 moles of LiOH. Now use this to work out the volume:

$$\text{Volume of LiOH} = \frac{\text{number of moles} \times 1000}{\text{concentration}}$$

$$= \frac{0.02912 \times 1000}{0.300} = 97.1 \text{ cm}^3$$

Figure 1: A titration where an alkali is being added to an acid. The indicator in the flask is phenolphthalein, so the solution starts colourless and turns pink at the end point.

Practice Questions — Application

Q1 18.8 cm³ of a 0.200 mol dm⁻³ solution of nitric acid (HNO_3) reacts with 0.450 mol dm⁻³ lithium hydroxide (LiOH) solution.

a) Write a balanced equation for this reaction.

b) Calculate the number of moles of HNO_3 present in the acid added.

c) How many moles of LiOH were in the sample of the alkali?

d) What volume of LiOH solution was required to neutralise the HNO_3 solution?

Q2 37.3 cm³ of a 0.420 mol dm⁻³ solution of potassium hydroxide (KOH) reacts with 1.10 mol dm⁻³ ethanoic acid (CH_3COOH) solution.

a) Write a balanced equation for this reaction.

b) Calculate the number of moles of KOH present in the alkali added.

c) What volume of CH_3COOH solution was required to neutralise the KOH solution?

Q3 14 cm³ of a 1.0 mol dm⁻³ $Ba(OH)_2$ solution reacts with a 0.50 mol dm⁻³ HCl solution. What volume of HCl solution was required to neutralise the $Ba(OH)_2$ solution?

Learning Objective:

- Be able to carry out calculations to determine the percentage yield of a reaction, or related quantities.

Specification Reference 2.1.3

5. Chemical Yield

If you're making a chemical (in a lab or a factory), it helps to know how much of it you can expect to get. In real life you'll never manage to make exactly that much — but percentage yield can give you an idea of how close you got.

Calculating theoretical yield

The **theoretical yield** is the mass of product that should be formed in a chemical reaction. It assumes no chemicals are 'lost' in the process. You can use the masses of reactants and a balanced equation to calculate the theoretical yield for a reaction. It's a bit like calculating reacting masses (see page 68) — here are the steps you have to go through:

1. Work out how many moles of the limiting reactant you have.
2. Use the equation to work out how many moles of product you would expect that much reactant to make.
3. Calculate the mass of that many moles of product — and that's the theoretical yield.

Tip: The limiting reactant is the one that you have a limited amount of (i.e. the reactant that's not in excess).

Example — Maths Skills

Ethanol can be oxidised to form ethanal:

$$C_2H_5OH + [O] \rightarrow CH_3CHO + H_2O$$

9.2 g of ethanol was reacted with an oxidising agent in excess. Calculate the theoretical yield of this reaction.

1. Ethanol is the limiting reactant so work out how many moles of ethanol you have:
   Molar mass of $C_2H_5OH = (2 \times 12) + (5 \times 1) + 16 + 1 = 46\text{ g mol}^{-1}$
   Number of moles C_2H_5OH = mass ÷ molar mass
   $= 9.2 \div 46 = 0.20$ moles.
2. Work out how many moles of product you would expect to make:
   From the equation, you know that 1 mole of C_2H_5OH produces 1 mole of CH_3CHO, so 0.20 moles of C_2H_5OH should produce 0.20 moles of CH_3CHO.
3. Now calculate the mass of that many moles of product:
   Molar mass of $CH_3CHO = (2 \times 12) + (4 \times 1) + 16 = 44\text{ g mol}^{-1}$
   Theoretical yield = number of moles × molar mass
   $= 0.20 \times 44 = 8.8$ g

Tip: The theoretical yield is the amount of product you would expect to form. The actual yield is the amount of product that is actually obtained.

Calculating percentage yield

For any reaction, the actual mass of product obtained (the actual yield) will always be less than the theoretical yield. There are many reasons for this. For example, sometimes not all the 'starting' chemicals react fully. And some chemicals are always 'lost', e.g. some solution gets left on filter paper, or is lost during transfers between containers. Once you've found the theoretical yield and the actual yield, you can work out the **percentage yield** — the actual amount of product you collect, written as a percentage of the theoretical yield. You can work out the percentage yield with this formula:

$$\text{Percentage Yield} = \frac{\text{Actual Yield}}{\text{Theoretical Yield}} \times 100$$

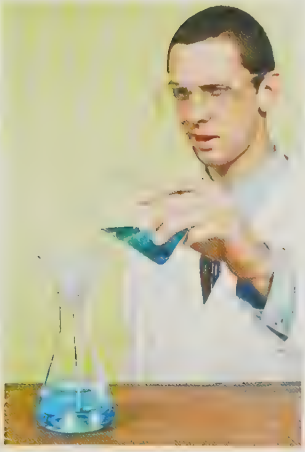


Figure 1: *A student pouring and filtering a solution. Some chemicals will be left on the glassware and some will be left on the filter paper.*

Examples — Maths Skills

In the ethanal example on the previous page, the theoretical yield was 8.80 g. Say you weighed the ethanal produced and found the actual yield was 2.10 g.

Then to work out the percentage yield you just have to plug the numbers into the formula:

$$\text{Percentage yield} = \frac{\text{Actual yield}}{\text{Theoretical yield}} \times 100$$

$$= (2.10 \div 8.80) \times 100 = 23.9\ \%$$

Here's another example:

5.00 g of ethanoyl chloride reacted with water to produce ethanoic acid. The theoretical yield of this reaction was 3.82 g. When the ethanoic acid was weighed it was found to have a mass of 2.46 g.

Calculate the percentage yield of this reaction.

All you need to do here is put the right numbers into the formula:

$$\text{Percentage yield} = \frac{\text{Actual yield}}{\text{Theoretical yield}} \times 100$$

$$= (2.46 \div 3.82) \times 100 = 64.4\%$$

Practice Questions — Application

Q1 The theoretical yield of a reaction used in an experiment was 3.24 g. The actual yield was 1.76 g. Calculate the percentage yield of the reaction.

Q2 In an experiment nitrobenzene was reduced to produce phenylamine. The theoretical yield of this reaction was 6.10 g. The phenylamine produced had a mass of 3.70 g. Calculate the percentage yield of this reaction.

Q3 3.00 g of ethanoic anhydride reacts with water to give ethanoic acid:

$$(CH_3CO)_2O + H_2O \rightarrow 2CH_3COOH$$

a) How many moles of ethanoic anhydride are there in 3.00 g?

b) Calculate the theoretical yield of ethanoic acid for this reaction.

c) Calculate the percentage yield if 2.80 g of ethanoic acid is made.

Q4 Propene reacts with HCl to produce 1-chloropropane:

$$CH_3CHCH_2 + HCl \rightarrow CH_3CH_2CH_2Cl$$

a) How much 1-chloropropane would you expect to get from 50.0 g of propene?

b) Calculate the percentage yield if only 54.0 g is made.

Q5 4.70 g of methanoic acid reacts to form 3.60 g of methanoic anhydride. The equation for this reaction is:

$$2HCOOH \rightarrow (CHO)_2O + H_2O$$

Calculate the percentage yield of this reaction.

Practice Questions — Fact Recall

Q1 What is meant by the 'theoretical yield' of a reaction?

Q2 Write down the formula for percentage yield.

Exam Tip

If you get a question in the exam on percentage yield and you've never heard of the compounds involved, don't be put off. You can just ignore the names — all you need are the theoretical and actual yields.

Exam Tip

This is a percentage yield, so it can never be more than 100%. If your answer is bigger than 100%, check the working for mistakes.

Exam Tip

Percentage yields can be calculated for organic or inorganic reactions. The method is exactly the same, so don't be put off if you're asked to calculate the percentage yield of an inorganic reaction in your exam.

Learning Objectives:

- Be able to calculate the atom economy of a reaction.
- Be able to discuss the benefits for sustainability of developing chemical processes with a high atom economy.

Specification Reference 2.1.3

6. Atom Economy

Atom economy is one way to work out how efficient a reaction is. Efficient reactions are better for the environment and save the chemical industry money.

What is atom economy?

The efficiency of a reaction is often measured by the percentage yield. This tells you how wasteful the process is — it's based on how much of the product is lost because of things like reactions not completing or losses during collection and purification. But percentage yield doesn't measure how wasteful the reaction itself is. A reaction that has a 100% yield could still be very wasteful if a lot of the atoms from the reactants wind up in by-products rather than the desired product. **Atom economy** is a measure of the proportion of reactant atoms that become part of the desired product (rather than by-products) in the balanced chemical equation.

Calculating atom economy

Atom economy is calculated using this formula:

$$\%\text{ atom economy} = \frac{\text{Molecular mass of desired product}}{\text{Sum of molecular masses of all products}} \times 100$$

Exam Tip

This is another equation you'll have to learn for your exam. Atom economy can never be more than 100%, so if you get answers over 100% (or less than 0%), then you've either got the equation wrong or you've slipped up in the calculation somewhere.

To calculate the atom economy for a reaction, you just need to find the molecular mass of the product you're interested in, add up the molecular masses of the products, and put them both into the formula.

Example

Bromomethane is reacted with sodium hydroxide to make methanol:

$$CH_3Br + NaOH \rightarrow CH_3OH + NaBr$$

Calculate the percentage atom economy for this reaction.

First, find the mass of the desired product — that's the methanol:

Mass of desired product = $12 + (3 \times 1) + 16 + 1 = 32$

Then, calculate the total mass of the products — add up the relative molecular masses of everything on the right side of the balanced equation:

Total mass of products = $32 + (23 + 79.9) = 134.9$

Now you can find the % atom economy:

$$\%\text{ atom economy} = \frac{\text{Molecular mass of desired product}}{\text{Sum of molecular masses of all products}} \times 100$$

$$= \frac{32}{134.9} \times 100 = 23.7\%$$

Figure 1: Tablets of the painkiller ibuprofen. Ibuprofen was originally made using a reaction with a 40% atom economy. Now a new way of making it with a 77% atom economy is used. This produces much less waste.

When you calculate the masses, you should use the number of moles of each compound that is in the balanced equation (e.g. the mass of '$2H_2$' should be $2 \times (2 \times 1) = 4$). Here's a quick example:

Example

Ethanol can be produced by fermenting glucose:

$$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$$

Calculate the percentage atom economy for this reaction.

First, find the mass of the desired product (2 moles of ethanol):

Mass of desired product = $2 \times ((12 \times 2) + (5 \times 1) + 16 + 1) = 92$

Then calculate the total mass of the products:

Total mass of products = $92 + 2(12 + (16 \times 2)) = 180$

$$\text{So, \% atom economy} = \frac{\text{Molecular mass of desired product}}{\text{Sum of molecular masses of all products}} \times 100$$

$$= \frac{92}{180} \times 100 = 51.1\%$$

Exam Tip
If you're asked to calculate atom economy in an exam, make sure that you start from the balanced equation.

Addition and substitution reactions

In an **addition reaction**, the reactants combine to form a single product. The atom economy for addition reactions is always 100% since no atoms are wasted.

Example

Ethene (C_2H_4) and hydrogen react to form ethane (C_2H_6) in an addition reaction: $C_2H_4 + H_2 \rightarrow C_2H_6$

The only product is ethane — the desired product. So no reactant atoms are wasted — the atom economy is 100%.

Tip: Any reaction where there's only one product will have a 100% atom economy because the mass of reactants has to equal the mass of product — atoms can't go anywhere else.

A **substitution reaction** is one where some atoms from one reactant are swapped with atoms from another reactant. This type of reaction always results in at least two products — the desired product and at least one by-product. So the atom economy of substitution reactions is always less than 100%.

Example

The reaction of bromoethane with sodium hydroxide to make methanol (on the previous page), is a substitution reaction and has a low atom economy.

Atom economy and percentage yield

Atom economy and percentage yield measure different things — so a reaction that has a high percentage yield might have a really low atom economy.

Example

0.475 g of CH_3Br reacts with an excess of NaOH in this reaction:

$$CH_3Br + NaOH \rightarrow CH_3OH + NaBr$$

0.153 g of CH_3OH is produced. What is the percentage yield?

Number of moles = mass of substance ÷ molar mass

Moles of $CH_3Br = 0.475 \div (12 + 3 \times 1 + 80) = 0.475 \div 95 = 0.005$ moles

The reactant : product ratio is 1 : 1, so the maximum number of moles of CH_3OH is 0.005.

Theoretical yield = $0.005 \times M_r(CH_3OH) = 0.005 \times (12 + (3 \times 1) + 16 + 1)$

$= 0.005 \times 32 = 0.160$ g

$$\text{percentage yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\% = \frac{0.153}{0.160} \times 100\% = 95.6\%$$

So this reaction has a very high percentage yield, but, as you saw on the previous page, the atom economy is low.

Tip: See pages 90-91 for more about calculating percentage yield.

Tip: If something is sustainable, it means it can occur over a long period of time, without damaging the atmosphere and environment, or depleting limited natural resources.

Atom economy in industry

HOW SCIENCE WORKS

Companies in the chemical industry will often choose to use reactions with high atom economies. High atom economy has environmental and economic benefits.

- Reactions with low atom economies are less sustainable. Many raw materials are in limited supply, so it makes sense to use them efficiently so they last as long as possible. Also, waste has to go somewhere — it's better for the environment if less is produced.
- A low atom economy means there's lots of waste produced. It costs money to separate the desired product from the waste products and more money to dispose of the waste products safely so they don't harm the environment. Companies will usually have paid good money to buy the reactant chemicals. It's a waste of money if a high proportion of them end up as useless products.

But reactions with a low atom economy may still be used if the waste products can be sold and used for something else (waste products like gases, salts and acids can often be useful reactants for other reactions).

Figure 2: *Chemical waste disposal site. Disposing of chemicals is expensive, so reactions with high atom economies and less waste are better in industry.*

Practice Questions — Application

Q1 Chlorine gas can react with excess methane to make chloromethane:

$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$$

a) Find the molecular mass of the chloromethane produced.

b) Find the total molecular mass of the products in this reaction.

c) Calculate the percentage atom economy of this reaction.

d) A company wants to use this reaction to make chloromethane, despite its low atom economy. Suggest one way that they could increase their profit and reduce the waste they produce.

Q2 Ethanol can be produced using this reaction:

$$C_2H_4 + H_2O \rightarrow C_2H_5OH$$

What is the percentage atom economy of this reaction?

Q3 Ethene can be produced from ethanol in a dehydration reaction:

$$C_2H_5OH \rightarrow C_2H_4 + H_2O$$

Calculate the percentage atom economy of this reaction.

Q4 In industry, ammonia (NH_3) is usually produced using this reaction:

Reaction 1: $N_2 + 3H_2 \rightarrow 2NH_3$

It can also be made using this reaction:

Reaction 2: $2NH_4Cl + Ca(OH)_2 \rightarrow CaCl_2 + 2NH_3 + 2H_2O$

a) Calculate the percentage atom economy of both reactions.

b) Give one reason why reaction 1 is used to produce ammonia industrially rather than reaction 2.

Practice Questions — Fact Recall

Q1 What is meant by the 'atom economy' of a reaction?

Q2 Write down the formula for calculating % atom economy.

Q3 Give two reasons why reactions with a low atom economy are not used in industry.

7. Oxidation Numbers

Oxidation numbers are really useful in chemistry. They help you work out what's going on in chemical reactions. You need to know how to assign oxidation numbers to atoms in elements, compounds and ions. This is done using a simple set of rules. Read on to find out more...

Assigning oxidation numbers

Atoms use electrons to form bonds with other atoms. The **oxidation number** of an element tells you the total number of electrons it has donated or accepted to form an ion or to form part of a compound. Oxidation numbers are also called oxidation states. There are lots of rules for working out oxidation numbers. Take a deep breath...

Uncombined elements have an oxidation number of 0 — they haven't accepted or donated any electrons. Elements just bonded to identical atoms also have an oxidation number of 0.

Examples

Uncombined elements — oxidation number = 0

Elements bonded to identical elements — oxidation number = 0

The oxidation number of a simple monatomic ion is the same as its charge.

Examples

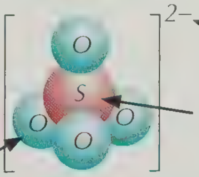
oxidation number = +1
Na+
Mg2+
oxidation number = +2

Monatomic ions

For molecular ions (see page 71), each of the constituent atoms has an oxidation number of its own and the sum of their oxidation numbers equals the overall oxidation number. This overall oxidation number is equal to the overall charge on the ion.

Example

Combined oxygen has an oxidation number of –2 (apart from in O_2 where it's 0). There are 4 oxygen atoms in SO_4^{2-}, so the total oxidation number from oxygens is 4 × –2 = –8.



Overall oxidation number is –2.

So the oxidation number of the sulfur is +6 (as –8 + 6 = –2).

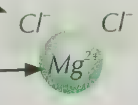
Figure 2: *Oxidation numbers of elements in the SO_4^{2-} ion.*

The sum of the oxidation numbers for a neutral compound is 0 (see Figure 3). If the compound is made up of more than one element, each element will have its own oxidation number.

Example

The oxidation number of the chloride ion is –1.

The oxidation number of the magnesium ion is +2.



The overall oxidation number of the compound is (2 × –1) + 2 = 0.

Figure 3: *Oxidation numbers of elements in magnesium chloride ($MgCl_2$).*

Learning Objectives:

- Be able to apply rules for assigning and calculating oxidation number for atoms in elements, compounds and ions.
- Be able to write formulas using oxidation numbers.
- Be able to use Roman numerals to indicate the magnitude of the oxidation number when an element may have compounds or ions with different oxidation numbers.

Specification Reference 2.1.5

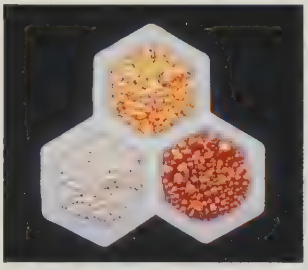


Figure 1: *Nuggets of gold, silver and copper. These are all uncombined elements with oxidation numbers of 0.*

Tip: All atoms are treated as ions when you're finding oxidation numbers, even if they're covalently bonded.

Tip: There are other exceptions for combined oxygen — in OF_2 it's +2, and in O_2F_2 it's +1.

Exam Tip
It's really important to remember the basic rules for working out oxidation numbers, as well as the exceptions — it's the kind of thing that could easily trip you up in exam questions.

Oxygen nearly always has an oxidation number of –2, except in peroxides (O_2^{2-}) where it's –1, and molecular oxygen (O_2) where it's 0.

Hydrogen always has an oxidation number of +1, except in metal hydrides (MH_x, M = metal) where it's –1 and in molecular hydrogen (H_2) where it's 0.

Examples

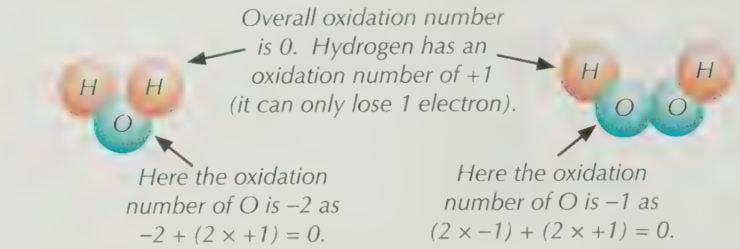

Overall oxidation number is 0. Hydrogen has an oxidation number of +1 (it can only lose 1 electron).
H
H
O
H
O
O
H
Here the oxidation number of O is –2 as $-2 + (2 \times +1) = 0$.
Here the oxidation number of O is –1 as $(2 \times -1) + (2 \times +1) = 0$.

Figure 4: Oxidation numbers of hydrogen and oxygen in water (H_2O) and hydrogen peroxide (H_2O_2).

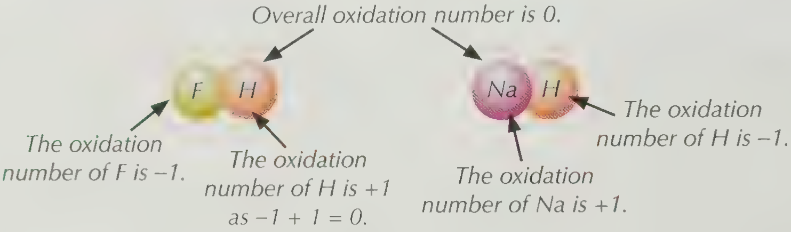

Overall oxidation number is 0.
F
H
Na
H
The oxidation number of F is –1.
The oxidation number of H is +1 as $-1 + 1 = 0$.
The oxidation number of Na is +1.
The oxidation number of H is –1.

Figure 5: Oxidation numbers of hydrogen in hydrogen fluoride (HF) and sodium hydride (NaH).

Finding oxidation numbers

You can work out oxidation numbers from formulas or systematic names.

Finding oxidation numbers from formulas

In your exam, you may get a question asking you to work out the oxidation number of one element in a compound. To do this you just have to follow all the rules on the previous page and above and you'll be fine.

Examples

Find the oxidation number of Zn in $Zn(OH)_2$.

- $Zn(OH)_2$ is neutral (it has no charge), so its overall oxidation number is 0.
- Oxygen's oxidation number is usually –2, and hydrogen's is usually +1.
- So the oxidation number of the $(OH)_2$ bit of the molecule is $2 \times (-2 + 1) = -2$.
- So the oxidation number of Zn in $Zn(OH)_2$ is $0 - (-2) = +2$.

Finding oxidation numbers from systematic names

If an element can have multiple oxidation numbers, or isn't in its 'normal' oxidation state, its oxidation number can be shown by using Roman numerals, e.g. (I) = +1, (II) = +2, (III) = +3 and so on. The Roman numerals are written after the name of the element they correspond to.

Examples

In iron(II) sulfate, iron has an oxidation number of +2. Formula = $FeSO_4$

In iron(III) sulfate, iron has an oxidation number of +3. Formula = $Fe_2(SO_4)_3$

COPPER (II) OXIDE CP
QTY 250g
Harmful

Figure 6: A bottle of copper(II) oxide. The Roman numerals show that the copper has an oxidation number of +2.

This is particularly useful when looking at -ate ions. Ions with names ending in -ate (e.g. sulfate, nitrate, carbonate) contain oxygen, as well as another element. For example, sulfates contain sulfur and oxygen, nitrates contain nitrogen and oxygen... and so on. But sometimes the 'other' element in the ion can exist with different oxidation numbers, and so form different '-ate ions'. You can use the systematic name to work out the formula of the ion.

Examples

In sulfate(VI) ions the sulfur has oxidation number +6. This is the SO_4^{2-} ion.

In sulfate(IV) ions, the sulfur has oxidation number +4. This is the SO_3^{2-} ion.

In nitrate(III), nitrogen has an oxidation number of +3. This is the NO_2^- ion.

Tip: The oxidation number in sulfate ions applies to the sulfur, not the oxygen, because oxygen always has an oxidation number of –2 in -ate ions.

Tip: Several ions have widely used common names that are different from their correct systematic names. E.g. the sulfate(IV) ion (SO_3^{2-}) is often called the sulfite ion.

Using oxidation numbers

If you know the oxidation numbers of the elements in a compound, you can use them to work out the systematic name for that compound or its formula.

Working out systematic names

You might have to work out the systematic name for a compound, given its formula. To do this you have to find the oxidation numbers of the elements in the compound and then add in Roman numerals where needed.

Examples

What is the systematic name of KNO_3?

This is potassium nitrate, but for the systematic name to be complete you need to give the oxidation number of the nitrogen. You know that potassium always forms K^+ ions, so the charge on the nitrate ion must be 1–.
Each oxygen atom in the NO_3^- ion has oxidation number –2.
This gives $3 \times -2 = -6$. Then, since the ion has an overall oxidation number of –1, the nitrogen must be in the +5 state.
So the compound is potassium nitrate(V).

What is the systematic name for ClO_2^-?

This formula contains chlorine and oxygen, so it's a chlorate.
Oxygen usually exists with an oxidation number of –2. There are 2 oxygens, so this will make the total charge from oxygens $-2 \times 2 = -4$.
The overall charge on the ion is –1, so chlorine must have an oxidation number of +3, since $-4 + 3 = -1$.
So, the systematic name is chlorate(III).

Tip: It'll help if you learn the charges of the three main -ate ions you'll come across in the exam. Sulfate ions (SO_4^{2-}) are always 2–, nitrate ions (NO_3^-) are always 1– and carbonate ions (CO_3^{2-}) are always 2–.

Figure 7: *Chlorates are powerful oxidising agents (see page 99). Potassium chlorate(V) is frequently used in pyrotechnics, such as fireworks.*

Working out formulas

You can also use oxidation numbers to work out the formula of a compound given its systematic name.

Example

What is the formula of iron(III) sulfate?

From the systematic name, you can tell iron has an oxidation number of +3.
The formula of the sulfate ion is SO_4^{2-} and it has an overall charge of –2.
The overall charge of the compound is 0, so you need to find a ratio of $Fe^{3+}:SO_4^{2-}$ that will make the overall charge 0.

$$(+3 \times 2) + (-2 \times 3) = 6 + -6 = 0$$

The ratio of $Fe:SO_4$ is 2:3.

So the formula is $Fe_2(SO_4)_3$.

Tip: Iron(III) sulfate is uncharged so has an overall oxidation number of 0.

Working out the formula of compound ions is just the same except the oxidation numbers won't add up to 0 — they'll add up to the charge of the ion instead. You'll be told the charge of the ion in the question.

Example

Find the formula of a phosphate(III) ion given that it has a charge of 3–.
As it's a phosphate ion it must contain phosphorus and oxygen. Oxygen has an oxidation number of –2 and you know from the systematic name that the phosphorus has an oxidation number of +3. The overall oxidation number of the ion is –3. So for the oxidation number to add up to –3 you need 3 oxygen atoms (giving a total of –6) and one phosphorus atom (+3). So the formula of a phosphate(III) ion is PO_3^{3-}.

Exam Tip
Don't forget to include the charge of the ion after you've worked out its formula. If you just put PO_3 here you wouldn't get any marks.

Practice Questions — Application

Q1 Give the oxidation numbers of the following ions.
a) Na^+ b) F^- c) Ca^{2+}

Q2 Give the overall oxidation numbers of the following ions.
a) OH b) CO_3^{2-} c) NO_3^-

Q3 Work out the oxidation numbers of all the elements in the following compounds and compound ions.
a) HCl b) CO_3^{2-} c) ClO_4^- d) HSO_4^-

Q4 Work out the oxidation numbers of carbon in the following.
a) CO b) CCl_4 c) $CaCO_3$ d) C_3H_6

Q5 Work out the oxidation numbers of phosphorus in the following.
a) P_4 b) PH_3 c) PO_4^{2-} d) P_2F_4

Q6 a) What is the oxidation number of iron in iron(III) chloride?
b) What is the oxidation number of chlorine in chlorate(VII) ions?

Q7 Give the systematic names of the following compounds.
a) $FeSO_4$ b) $MnCO_3$ c) CuO

Q8 Give the formulas of the following compounds and compound ions.
a) Copper(II) sulfate.
b) Iron(II) oxide.
c) Nitrate(III) ions with an overall charge of –1.
d) Chromate(VI) ions with an overall charge of –2.

Exam Tip
Finding oxidation numbers is easy when you know how. Just make sure you learn the rules for the exam and you'll be fine.

Practice Questions — Fact Recall

Q1 Give the oxidation number of an element bonded to an identical atom.

Q2 What is the sum of the oxidation numbers for a neutral compound?

Q3 What is the oxidation number of oxygen in a peroxide?

Q4 Give the oxidation number of hydrogen in a metal hydride.

8. Redox Reactions

This'll probably ring a bell from GCSE, but don't go thinking you know it all already — there's plenty to learn about redox reactions.

Learning Objectives:

- Be able to describe the terms oxidation and reduction in terms of electron transfer and changes in oxidation number.
- Know the redox reactions of metals with acids to form salts, including full equations.
- Be able to interpret redox equations and unfamiliar redox reactions to make predictions in terms of oxidation numbers and electron loss and gain.

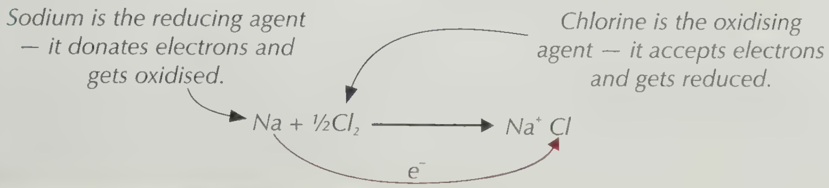
Specification Reference 2.1.5

What are redox reactions?

A loss of electrons is called **oxidation**. A gain in electrons is called **reduction**. Reduction and oxidation happen simultaneously — hence the term "**redox**" reaction. An **oxidising agent** accepts electrons and gets reduced. A **reducing agent** donates electrons and gets oxidised.

Example

Here's a redox reaction between sodium and chlorine to form sodium chloride:



Sodium is the reducing agent — it donates electrons and gets oxidised.

Chlorine is the oxidising agent — it accepts electrons and gets reduced.

$Na + \tfrac{1}{2}Cl_2 \longrightarrow Na^+Cl^-$

Changing oxidation numbers

Oxidation numbers go up or down as electrons are lost or gained.

- The oxidation number for an atom will increase by 1 for each electron lost.
- The oxidation number will decrease by 1 for each electron gained.

When metals form compounds, they generally donate electrons to form positive ions — this is accompanied by an increase in oxidation number. When non-metals form compounds, they generally gain electrons and form negative ions — this is accompanied by a decrease in oxidation number.

Examples

Zinc (a metal) can lose electrons to form Zn^{2+} ions. When this happens, its oxidation number increases from 0 to +2.

Bromine (a non-metal) can gain an electron to form Br^- ions. When this happens, its oxidation number decreases from 0 to –1.

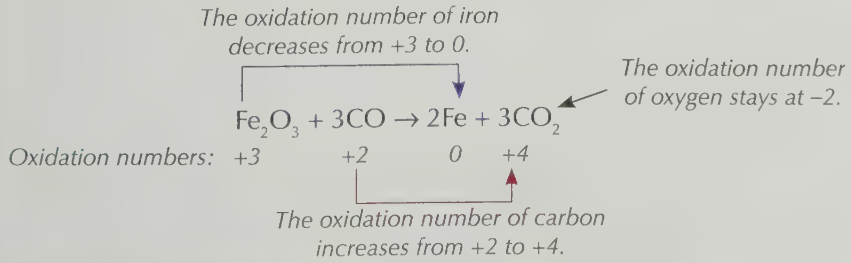
Tip: Now's your chance to learn the most famous memory aid thingy in the world...

OIL RIG
Oxidation Is Loss
Reduction Is Gain
(of electrons)

In a redox reaction, some oxidation numbers will change — something will lose electrons and end up with an increased oxidation number and something will gain electrons and end up with a decreased oxidation number.

Example

In this reaction between iron(III) oxide and carbon(II) oxide (a.k.a. carbon monoxide), the products are the element iron and carbon(IV) oxide (more commonly known as carbon dioxide).



The oxidation number of iron decreases from +3 to 0.

The oxidation number of oxygen stays at –2.

$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$

Oxidation numbers: +3 +2 0 +4

The oxidation number of carbon increases from +2 to +4.

Tip: When an element is reduced, it's oxidation number is also reduced.

Tip: Look back at the rules for assigning oxidation numbers on pages 95-96 if you're unsure about this.

Tip: Remember — oxidising agents get reduced while reducing agents get oxidised.

Once you have identified how the oxidation numbers of elements and ions change in a reaction, you can work out which substance in a reaction acts as a reducing or oxidising agent.

Examples

Identify the oxidising and reducing agents in this reaction:
$4Fe + 3O_2 \rightarrow 2Fe_2O_3$

Iron has gone from having an oxidation number of 0 to an oxidation number of +3. It's lost electrons and has been oxidised. This makes it the reducing agent in this reaction.

Oxygen has gone from having an oxidation number of 0 to an oxidation number of –2. It's gained electrons and has been reduced. This means it's the oxidising agent in this reaction.

Identify the oxidising and reducing agents in this reaction:
$2Na + Cl_2 \rightarrow 2NaCl$

Sodium has gone from having an oxidation number of 0 to an oxidation number of +1. It's lost an electron and has been oxidised, so it's a reducing agent.

Chlorine has gone from having an oxidation number of 0 to an oxidation number of –1. It's gained an electron and has been reduced, so it's an oxidising agent.

When asked about oxidation and reduction, it's always worth working out the oxidation numbers of each atom or ion to see exactly how the electrons are moving around. But as a rule:

- When metals form compounds, they generally donate electrons to form positive ions — meaning they usually have positive oxidation numbers.
- When non-metals form compounds, they generally gain electrons — meaning they usually have negative oxidation numbers.

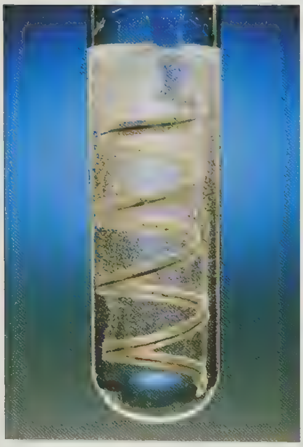


Figure 1: Magnesium ribbon reacting with hydrochloric acid. The bubbles are the hydrogen gas molecules that are being formed.

Reactions of dilute acids with metals

On page 79 you saw how metals react with acids to produce a salt and hydrogen gas. Well this is a redox reaction. The metal atoms are oxidised, losing electrons to form positive metal ions (in salts). The hydrogen ions in solution are reduced, gaining electrons and forming hydrogen molecules.

Example

Magnesium reacts with dilute hydrochloric acid like this:

The oxidation number of magnesium increases from 0 to +2.

The oxidation number of chlorine stays at –1.

$$Mg_{(s)} + 2HCl_{(aq)} \rightarrow MgCl_{2(aq)} + H_{2(g)}$$

Oxidation numbers: 0 +1 +2 0

The oxidation number of hydrogen decreases from +1 to 0.

Example

If you use sulfuric acid instead of hydrochloric acid, exactly the same processes of oxidation and reduction take place.

Potassium is oxidised to K⁺ ions in the reaction with dilute sulfuric acid like this:

The oxidation number of potassium increases from 0 to +1.

The oxidation number of SO_4 stays at −2 .

$$\begin{array}{lccccccc} & 2K_{(s)} & + & H_2SO_{4(aq)} & \rightarrow & K_2SO_{4(aq)} & + & H_{2(g)} \\ \textit{Oxidation numbers:} & 0 & & +1 & & +1 & & 0 \end{array}$$

The oxidation number of hydrogen decreases from +1 to 0.

Practice Questions — Application

Q1 Describe the changes in oxidation number that occur in each of the following reactions between metals and acids.

- a) $Mg + H_2SO_4 \rightarrow MgSO_4 + H_2$
- b) $2V + 6HCl \rightarrow 2VCl_3 + 3H_2$
- c) $2Fe + 3H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 3H_2$

Q2 This is a redox reaction: $MnO_2 + 4HCl \rightarrow MnCl_2 + Cl_2 + 2H_2O$

- a) Describe the changes in oxidation number that occur in this reaction.
- b) Identify the oxidising and reducing agents in this reaction.

Practice Questions — Fact Recall

Q1 What is oxidation?

Q2 What is reduction?

Q3 Describe the role of an oxidising agent in a redox reaction.

Q4 Describe the role of a reducing agent in a redox reaction.

Q5 What happens to the oxidation number when an atom loses an electron?

Q6 What happens to the oxidation number when an atom gains an electron?

Tip: If you're asked to describe the changes in oxidation number in a reaction you have to say which elements change oxidation numbers and what the change is.

Tip: The oxidation number of an atom doesn't always change when it reacts, so don't be alarmed if your answer is the same for the beginning and end of the reaction.

Section Summary

Make sure you know...

- That acids release protons in aqueous solution and bases absorb H^+ ions in aqueous solution.
- That alkalis are soluble bases that release OH^- ions in aqueous solution.
- The formulas of the common acids HCl, H_2SO_4, HNO_3 and CH_3COOH.
- The formulas of the common alkalis NaOH, KOH and NH_3.
- The definition and nature of strong and weak acids and bases.
- That a salt is produced when the H^+ ion in an acid is replaced by a metal ion or NH_4^+.
- That in neutralisation reactions between acids and bases, H^+ ions from the acid and OH^- ions from the base react together to form water.
- That metal oxides, metal hydroxides and ammonia can all act as bases.
- That acids react with bases, alkalis, metals and metal carbonates to form salts.
- What the terms anhydrous, hydrated and water of crystallisation mean in terms of salts.
- How to calculate the formula of a hydrated salt from mass compositions or percentage compositions.
- How to perform acid-base titrations and carry out structured titrations.
- Some of the appropriate indicators used for acid-base titrations.
- The techniques for precisely measuring the masses of solids, and the volumes of liquids and gases.
- The procedure for making a standard solution from a solid and from a more concentrated solution.
- How to calculate unknown concentrations and volumes using data collected from a titration.
- How to calculate the percentage yield of a reaction, from the chemical equation.
- How to calculate atom economy from a chemical equation.
- The industrial advantages of using reactions with high atom economies, in terms of cost and sustainability.
- How to assign oxidation numbers to atoms in elements, compounds and ions.
- How to use Roman numerals to determine the oxidation number of an element in a compound.
- How to write formulas using oxidation numbers.
- That oxidation is a loss of electrons and reduction is a gain in electrons.
- That oxidation and reduction result in changes in oxidation number.
- How to interpret redox equations and redox reactions to make predictions about oxidation numbers and about electron loss and gain.

Exam-style Questions

1 What is the formula of iron(III) sulfate?

A $FeSO_4$

B $Fe(SO_4)_2$

C Fe_2SO_4

D $Fe_2(SO_4)_3$

(1 mark)

2 Which of these equations **does not** show a redox reaction?

A $Mg + 2HCl \rightarrow MgCl_2 + H_2$

B $Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$

C $Ca(OH)_2 + 2HCl \rightarrow CaCl_2 + 2H_2O$

D $Ag + H_2S \rightarrow Ag_2S + H_2$

(1 mark)

3 What is the oxidation number of chromium in the compound $Cr_2(SO_4)_3$?

A +3

B +2

C –3

D +1

(1 mark)

4 **(a)** Silicon is most commonly found as silicon dioxide (SiO_2).

(i) State the oxidation state of silicon in SiO_2.

(1 mark)

(ii) Give the systematic name of silicon dioxide.

(1 mark)

(b) Silicon dioxide reacts with sodium hydroxide (NaOH), as shown by the equation below.

$$SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O$$

Use your knowledge of oxidation states to determine whether the reaction above is a redox reaction. Explain you answer.

(2 marks)

5 Hydrogen can be made by reacting a metal with an acid.

(a) Zinc metal and hydrochloric acid are reacted together.

(i) Write a balanced equation to show the reaction between zinc and hydrochloric acid. You should include state symbols in your answer.

(2 marks)

(ii) Use your answer to **(i)** to calculate the atom economy for this reaction.

(2 marks)

(b) Hydrogen is produced on an industrial scale through steam reformation. This involves reacting methane with steam.

$$CH_{4(g)} + H_2O_{(g)} \rightarrow CO_{(g)} + 3H_{2(g)}$$

(i) What is the atom economy of the reaction above?

(2 marks)

(ii) With reference to your answers to **a (ii)** and **b (i)**, suggest two reasons why steam reformation is preferred as a method for producing hydrogen, compared to reacting a metal with an acid.

(2 marks)

6 A student is doing an experiment into *water of crystallisation*. She heats an 8.93 g sample of *hydrated* iron(II) sulfate to form 4.88 g of *anhydrous* iron(II) sulfate.

(a) Define the following terms:

(i) *water of crystallisation.*

(ii) *hydrated.*

(iii) *anhydrous.*

(3 marks)

(b) What is the oxidation number of iron in the hydrated iron(II) sulfate compound?

(1 mark)

(c) The formula of the hydrated iron complex can be expressed as $FeSO_4\bullet\mathbf{x}H_2O$,where **x** represents a whole number. Find the value of **x** and write the formula of the hydrated salt.

(3 marks)

7 This question is about the reactions of acids.

(a) When an acid is added to a base, a neutralisation reaction occurs. In a titration, 26.0 cm^3 of 0.600 mol dm^{-3} hydrochloric acid was needed to exactly neutralise 20.0 cm^3 of a sodium hydroxide solution.

(i) Write an equation for the reaction between hydrochloric acid and sodium hydroxide. Include state symbols in your answer.

(2 marks)

(ii) Calculate how many moles of hydrochloric acid were added to the sodium hydroxide solution.

(2 marks)

(iii) Calculate the concentration of the sodium hydroxide solution used in this titration.

(2 marks)

(b) Acids react with metals to produce salts. When aluminium (Al) reacts with hydrochloric acid, aluminium(III) chloride is produced.

(i) What is the oxidation number of aluminium in aluminium(III) chloride?

(1 mark)

(ii) Use your knowledge of oxidation numbers to work out the chemical formula of aluminium(III) chloride.

(1 mark)

(c) The reactions of acids with metals are redox reactions. Below is the reaction of sodium with sulfuric acid:

$$2Na + H_2SO_4 \rightarrow Na_2SO_4 + H_2$$

(i) How does the oxidation number of sodium change during this reaction?

(1 mark)

(ii) What is the role of sodium in this reaction?

(1 mark)

(d) The reaction of dilute nitric acid with calcium produces a salt called calcium nitrate ($Ca(NO_3)_2$).
Hydrated calcium(II) nitrate contains 30.5% water by mass.
The hydrated salt has the formula $Ca(NO_3)_2.\mathbf{x}H_2O$. Find the value of **x**.

(4 marks)

(e) A student wants to make 250 cm^3 of a standard solution of calcium(II) nitrate. He uses a volumetric flask to accurately measure 250 cm^3 of water and adds it to a beaker containing the correct mass of calcium(II) nitrate, dissolved in water. What has the student done wrong and how will this error affect the concentration of the standard solution made?

(2 marks)

Module 2 Section 4: Electrons, Bonding and Structure

1. Electronic Structure

Learning Objectives:

- Know how many orbitals make up the s, p and d sub-shells and how many electrons can fill s, p and d sub-shells.
- Recall how many electrons can fill the first four shells.
- Understand that atomic orbitals are a region around the nucleus that can hold up to two electrons, with opposite spins.
- Know the shapes of s- and p-orbitals.
- Understand that electrons fill the first three shells and the 4s and 4p orbitals in order of increasing energy.
- Know that electrons occupy orbitals of the same energy singly before pairing.
- Deduce the electron configurations of atoms, given their atomic number, up to $Z = 36$ and ions, given their atomic number and ionic charge, limited to s- and p-block ions, up to $Z = 36$.

Specification Reference 2.2.1

Electronic structure is all about how electrons are arranged in atoms.

Electron shells

In the currently accepted model of the atom, electrons have fixed energies. They move around the nucleus in certain regions of the atom called **shells** or **energy levels**. Each shell is given a number called the principal quantum number. The further a shell is from the nucleus, the higher its energy and the larger its principal quantum number — see Figure 1.

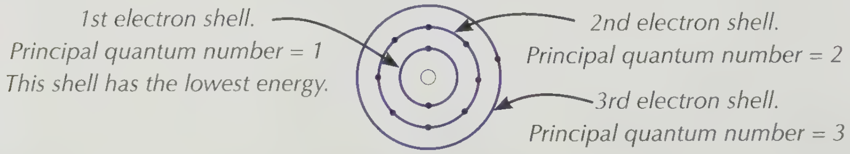

1st electron shell.
Principal quantum number = 1
This shell has the lowest energy.
2nd electron shell.
Principal quantum number = 2
3rd electron shell.
Principal quantum number = 3

***Figure 1**: A sodium atom.*

These shells are divided up into **sub-shells**. Different electron shells have different numbers of sub-shells, which each have a different energy. Sub-shells can be s sub-shells, p sub-shells, d sub-shells or f sub-shells.

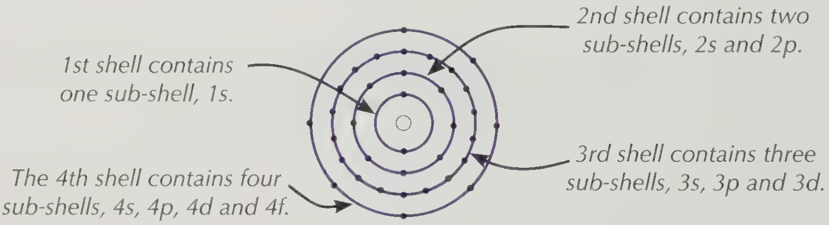

1st shell contains one sub-shell, 1s.
2nd shell contains two sub-shells, 2s and 2p.
The 4th shell contains four sub-shells, 4s, 4p, 4d and 4f.
3rd shell contains three sub-shells, 3s, 3p and 3d.

***Figure 2**: A bromine atom.*

These sub-shells have different numbers of **orbitals** which can each hold up to 2 electrons. The table below shows the number of orbitals and electrons in each sub-shell. You can use it to work out how many electrons each shell can hold.

Sub-shell	Number of orbitals	Maximum electrons
s	1	2
p	3	6
d	5	10
f	7	14

***Figure 3**: The number of electrons that can fill each sub-shell.*

Example

The third shell contains 3 sub-shells: 3s, 3p and 3d.

- An s sub-shell contains 1 orbital, so can hold 2 electrons (1 × 2).
- A p sub-shell contains 3 orbitals, so can hold 6 electrons (3 × 2).
- A d sub-shell contains 5 orbitals, so can hold 10 electrons (5 × 2).

So the total number of electrons the third shell can hold is 2 + 6 + 10 = **18**.

Tip: Don't get confused by notation like 2s or 4f. The letter shows what type of sub-shell it is, the number shows what shell it's in. So 3p means a p sub-shell in the 3rd electron shell.

The table on the right shows the number of electrons that the first four electron shells can hold.

Shell	Sub-shells	Total number of electrons
1st	1s	2 = 2
2nd	2s 2p	2 + (3 × 2) = 8
3rd	3s 3p 3d	2 + (3 × 2) + (5 × 2) = 18
4th	4s 4p 4d 4f	2 + (3 × 2) + (5 × 2) + (7 × 2) = 32

Orbital shapes

An orbital is the bit of space that an electron moves in (see Figure 4). Orbitals within the same sub-shell have the same energy. If there are two electrons in an orbital, they must '**spin**' in opposite directions — this is called spin-pairing.

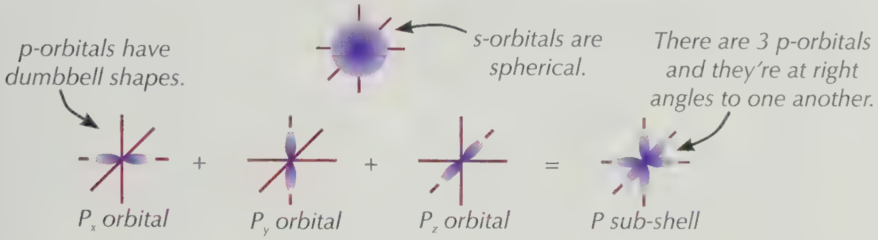
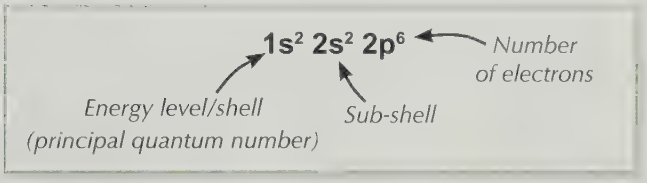

p-orbitals have dumbbell shapes.
s-orbitals are spherical.
There are 3 p-orbitals and they're at right angles to one another.
+
+
=
P_x orbital
P_y orbital
P_z orbital
P sub-shell

Figure 4: *s- and p-orbitals.*

Showing electron configurations

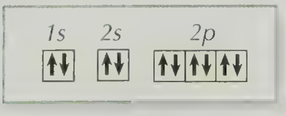
The number of electrons that an atom or ion has, and how they are arranged, is called its **electron configuration**. Electron configurations can be shown in different ways. For example, an atom of neon has 10 electrons — two electrons are in the 1s sub-shell, two are in the 2s sub-shell and six are in the 2p sub-shell. You can show this electron configuration in three different ways...

1. Sub-shell notation


$1s^2\ 2s^2\ 2p^6$
Number of electrons
Energy level/shell (principal quantum number)
Sub-shell

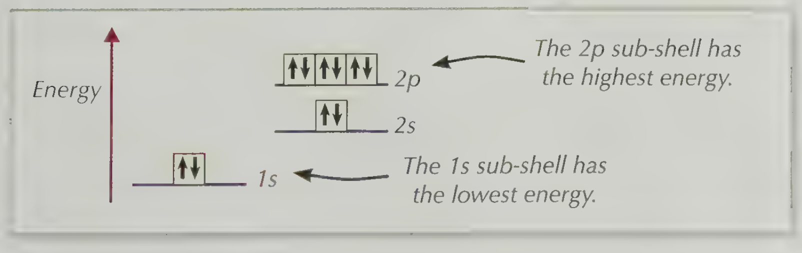
2. Electrons in boxes

Each of the boxes represents one orbital. Each of the arrows represents one electron. The up and down arrows represent the electrons spinning in opposite directions. Two electrons can only occupy the same orbital if they have opposite spin.



3. Energy level diagrams

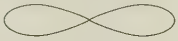
These show the energy of the electrons in different orbitals, as well as the number of electrons and their arrangement.


Energy
2p
2s
1s
The 2p sub-shell has the highest energy.
The 1s sub-shell has the lowest energy.

Exam Tip
Make sure you learn how many electrons each electron shell can hold — you won't get far with electronic structures if you don't know these numbers.

Tip: Electrons have a property called 'spin'. Spin just has to do with the momentum that an electron has (and that's all you need to know about it for now). Two electrons in the same orbital will have opposite spins — one is called 'down' and the other 'up'.

Tip: Dumbbell-shaped just means it looks like this:



So if you're asked to draw the shape of a p-orbital, draw this.

Exam Tip
In the exam you'll only have to do electron configurations up to the d sub-shell (so don't worry about the f sub-shell).

Exam Tip
Electron configurations are normally shown using sub-shell notation or electrons in boxes, so make sure you're confident using both these methods.

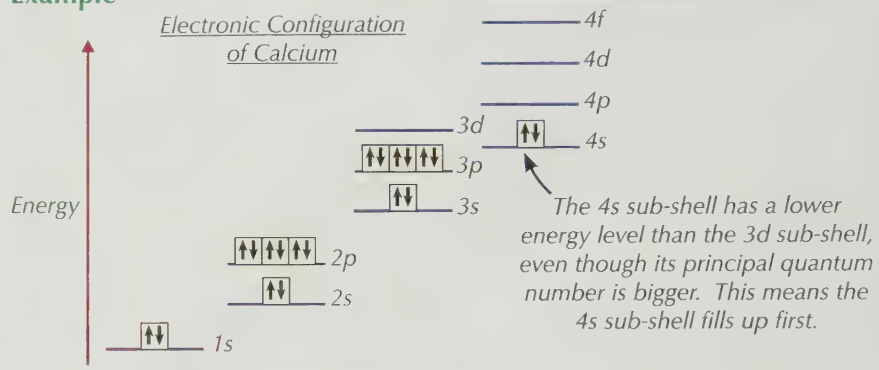
Working out electron configurations

You can figure out most electronic configurations pretty easily, so long as you know a few simple rules:

Rule 1

Electrons fill up the lowest energy sub-shells first.

Example



The 4s sub-shell has a lower energy level than the 3d sub-shell, even though its principal quantum number is bigger. This means the 4s sub-shell fills up first.

Tip: Even though the 4s sub-shell fills up before the 3d sub-shell, the 3d electrons are usually shown first when you write the configurations down. So the electron configuration of Ca is usually shown as:

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$

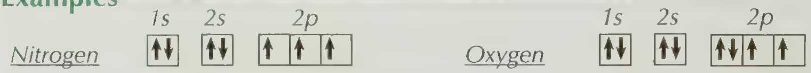
and the electron configuration of Sc is:

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^1\ 4s^2$

Rule 2

Electrons fill orbitals with the same energy singly before they start sharing.

Examples



Tip: Elements with their outer electrons in an s sub-shell are called s block elements. Elements with their outer electrons in a p sub-shell are called p-block elements.

Rule 3

For the configuration of ions from the s and p blocks of the periodic table, just add or remove the electrons to or from the highest energy occupied sub-shell.

Examples

Mg atom: $1s^2\ 2s^2\ 2p^6\ 3s^2$

Mg^{2+} ion: $1s^2\ 2s^2\ 2p^6$

Cl atom: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$

Cl^- ion: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$

Shortened electron configurations

Noble gas symbols in square brackets, such as [Ar], are sometimes used in electron configurations. For example, calcium ($1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$) can be written as $[Ar]4s^2$, where $[Ar] = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$.

Theories of electronic structure

HOW SCIENCE WORKS

You saw on pages 42-44 that it took a long time for our current theory of the structure of the atom to be developed. It took scientists even longer to work out how the electrons were arranged.

The Bohr model (see pages 43-44) was a good starting point. It proposed that electrons orbit the nucleus in spherical shells with fixed energy levels. The model helped to explain why atoms only absorb or emit energy at certain frequencies (see Figure 5) — these are the frequencies that correspond to the energy difference between two of the energy levels.

Whilst the Bohr model is a good approximation, it doesn't explain some of the finer details of absorption and emission spectra. The model was later refined so that the shells didn't have to be spherical. This caused the idea of sub-shells and orbitals to be developed.

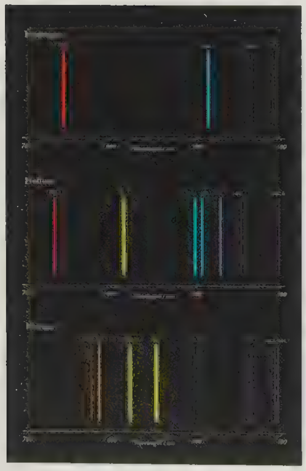


Figure 5: *The emission spectra of hydrogen, helium and mercury show distinct lines corresponding to the differences in energy between electron shells.*

In 1927, Werner Heisenberg came up with the theory that you cannot know the speed of an electron and its exact position at the same time — this is known as Heisenberg's uncertainty principle. As a result, scientists now think of orbitals as an area where electrons are most likely to be found, rather than where they will definitely be.

Investigations into electronic structure has led to the development of an area of science called quantum mechanics. This uses maths to explain how very small particles, such as electrons, behave. It's also allowed scientists to develop theories that explain and predict the properties of atoms, such as their spectra and the way they bond to other atoms to form molecules.

Figure 6: *Werner Heisenberg was a German scientist who helped to develop the model of electronic structure scientists use today.*

Practice Questions — Application

Q1 Use sub-shell notation to show the full electron configurations of the elements listed below.

a) Lithium b) Titanium

c) Gallium d) Nitrogen

Q2 Draw arrows in boxes to show the electron configurations of the elements listed below.

a) Calcium b) Nickel

c) Sodium d) Oxygen

Q3 Draw energy level diagrams to show the electron configurations of the elements listed below.

a) Magnesium b) Argon

c) Carbon d) Arsenic

Q4 Use sub-shell notation to show the electron configurations of the ions listed below.

a) Na^+ b) O^{2-}

c) Al^{3+} d) Cl^-

Q5 Which elements have the electron configurations given below?

a) $[Ar]3d^{10}\,4s^2\,4p^5$

b) $[Ne]3s^2\,3p^3$

c) $[Ar]3d^3\,4s^2$

Exam Tip

Writing electron configurations using noble gas symbols can save you loads of time. Just make sure you've got your head round sub-shell notation before you start to use it — otherwise you're likely to get confused. And if a question asks you to give the full configuration then make sure that's what you do.

Practice Questions — Fact Recall

Q1 How many orbitals does a p sub-shell contain?

Q2 How many electrons can a p sub-shell hold?

Q3 How many electrons can the 3rd electron shell hold in total?

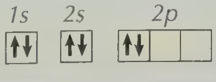
Q4 Describe the shape of:

a) an s-orbital. b) a p-orbital.

Q5 What does "electron configuration" mean?

Q6 Which electron shells are filled up first?

Q7 The electron configuration shown below is wrong. Explain why.



Learning Objectives:

- Describe the term ionic bonding as the electrostatic attraction between positive and negative ions.
- Be able to construct 'dot-and-cross' diagrams for ionic compounds.
- Explain that the solid structures of giant ionic lattices result from oppositely charged ions strongly attracted in all directions, e.g. NaCl.
- Explain the effect of structure and bonding on the physical properties of ionic compounds, including melting and boiling points, solubility and electrical conductivity in solid, liquid and aqueous states.

Specification Reference 2.2.2

2. Ionic Bonding

When atoms join together, they form a bond. There are two main types of bonding — ionic and covalent. First up is ionic bonding.

Ionic compounds

Ions form when atoms lose or gain electrons to become positively or negatively charged. **Electrostatic attraction** holds positive and negative ions together — it's very strong. When atoms are held together like this, it's called ionic bonding. So, an **ionic bond** is an electrostatic attraction between two oppositely charged ions.

When oppositely charged ions form an ionic bond you get an **ionic compound**. The formula of a compound tells you what ions that compound has in it. The positive charges in the compound balance the negative charges exactly — so the total overall charge is zero. This is a dead handy way of checking the formula.

Example

In the compound Fe_2O_3, there are three oxygen ions, each with a charge of –2. So the total negative charge is $3 \times (-2) = -6$.

To balance this out and make the compound neutral, the two iron ions must have a combined charge of +6.

So each iron ion has a charge of $(+6) \div 2 = +3$.

Figure 1: The reaction between sodium and chlorine to form sodium chloride.

Dot-and-cross diagrams

You can use 'dot-and-cross' diagrams to show how ionic bonding works in ionic compounds. Dot-and-cross diagrams show the arrangement of electrons in an atom or ion. Each electron is represented by a dot or a cross. They can also show which atom the electrons in a bond originally came from.

Examples

Sodium chloride

The formula of sodium chloride is NaCl. It just tells you that sodium chloride is made up of Na^+ ions and Cl^- ions (in a 1:1 ratio). In NaCl, the single positive charge on the Na^+ ion balances the single negative charge on the Cl^- ion (see Figure 2).

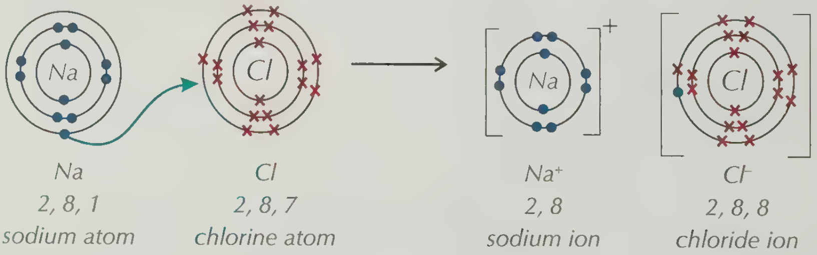


Figure 2: Formation of sodium chloride from a sodium atom and a chlorine atom.

Here the dots represent the Na electrons and the crosses represent the Cl electrons. All electrons are really identical, but this is a good way of following their movement. It's clear to see how the sodium atom loses an electron to form a sodium ion (Na^+), whilst the chlorine atom gains an electron to form a chloride ion (Cl^-). Both the ions have full outer shells.

Magnesium oxide

Magnesium oxide, MgO, is another example of an ionic compound. The formation of magnesium oxide involves the transfer of two electrons — see Figure 3. The formula tells you that magnesium oxide is made up of Mg^{2+} ions and O^{2-} ions in a 1:1 ratio. Figure 3 shows outer electrons only.

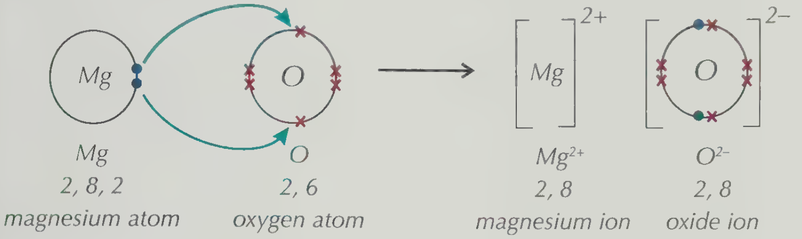

Mg
O
Mg
2+
O
2–
Mg
2, 8, 2
magnesium atom
O
2, 6
oxygen atom
Mg²⁺
2, 8
magnesium ion
O²⁻
2, 8
oxide ion

Figure 3: *Formation of magnesium oxide from a magnesium atom and an oxygen atom.*

Magnesium chloride

Magnesium chloride ($MgCl_2$) is different again. In this compound, the 2+ charge on the Mg^{2+} ion balances the two individual charges on the two Cl^- ions — see Figure 4.

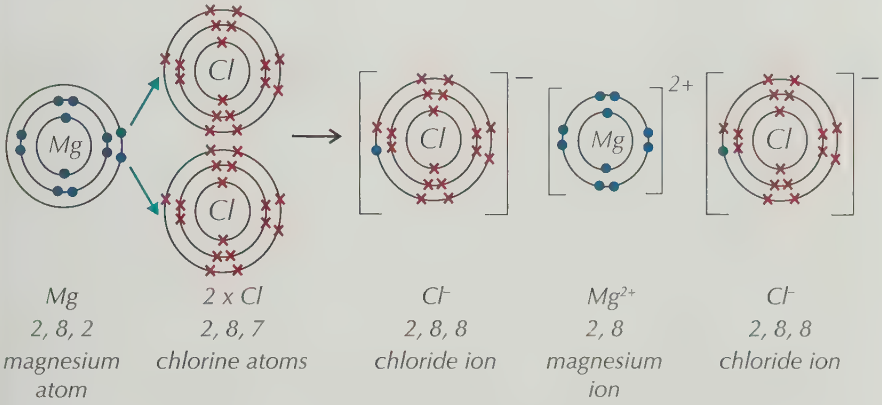
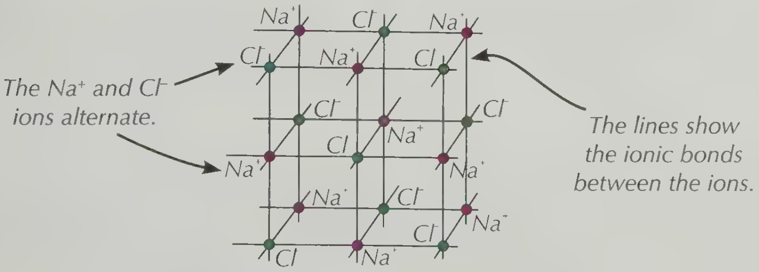

Mg
Cl
Cl
Cl
–
Mg
2+
Cl
–
Mg
2, 8, 2
magnesium atom
2 x Cl
2, 8, 7
chlorine atoms
Cl⁻
2, 8, 8
chloride ion
Mg²⁺
2, 8
magnesium ion
Cl⁻
2, 8, 8
chloride ion

Figure 4: *Formation of magnesium chloride from a magnesium atom and two chlorine atoms.*

Giant ionic lattices

Ionic crystals are **giant lattices** of ions. A lattice is just a regular structure. The structure's called 'giant' because it's made up of the same basic unit repeated over and over again. It forms because each ion is electrostatically attracted in all directions to ions of the opposite charge. The sodium chloride lattice is cube shaped (see Figures 5 and 6).


Na⁺
Cl⁻
Na⁺
Cl⁻
Na⁺
Cl⁻
Cl⁻
Cl⁻
Cl⁻
Na⁺
Na⁺
Na⁺
Na⁺
Cl⁻
Cl⁻
Na⁺
Cl⁻
Na⁺

The Na⁺ and Cl⁻ ions alternate.

The lines show the ionic bonds between the ions.

Figure 5: *The structure of sodium chloride.*

Different ionic compounds have different shaped structures, but they're all still giant lattices.

Tip: You can often use an atom's position in the periodic table to predict what charge ion it will form — atoms in the s-block will lose electrons, and atoms in the p-block will normally gain or lose electrons until they have a full outer shell (see page 71).

Exam Tip

You can simplify dot-and-cross diagrams by only showing the outer shell of electrons on each atom (see Figure 3). Most of the time it doesn't matter if dot-and-cross diagrams show all the shells or just the outer ones, but if you're asked to draw them a certain way in the exam then make sure you do.

Figure 6: *Crystals of sodium chloride (table salt).*

Exam Tip
Make sure you learn these — you might get asked what properties you'd expect a specific ionic compound to have in the exam. It doesn't matter if you've never heard of the compound before — if you know it's an ionic compound you know it'll have these properties.

Tip: These physical properties are sometimes called 'macroscopic' properties — that's just a fancy way of saying properties that result from lots of particles interacting with each other. For example, you couldn't say an individual atom has a melting point, but a compound made up of lots of atoms does. You should be able to explain how ionic bonds cause the macroscopic properties of ionic compounds.

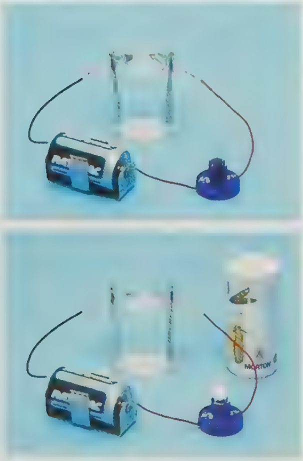


Figure 7: *Water doesn't conduct electricity (see top). When the ionic compound sodium chloride is added to the water (above), it dissolves and the free Na^+ and Cl^- ions allow a current to flow.*

Behaviour of ionic compounds

HOW SCIENCE WORKS

The structure and bonding of ionic compounds decides their physical properties — things like their electrical conductivity, melting point and solubility.

Electrical conductivity

Ionic compounds conduct electricity when they're molten or dissolved — but not when they're solid. The ions in a liquid are free to move (and they carry a charge). In a solid they're fixed in position by the strong ionic bonds.

Melting and boiling points

Ionic compounds have high melting and boiling points. The giant ionic lattices are held together by strong electrostatic forces. It takes loads of energy to overcome these forces, so melting and boiling points are very high (801 °C and 1413 °C respectively for sodium chloride).

Solubility

Ionic compounds tend to dissolve in water. Water molecules are polar — part of the molecule has a small negative charge, and the other bits have small positive charges (see page 121). The water molecules pull the ions away from the lattice and cause it to dissolve.

Practice Questions — Application

Q1 Fluorine and lithium react together to form lithium fluoride, an ionic compound that contains F^- and Li^+ ions.

- a) Give the formula of the compound formed.
- b) Describe how an ionic bond forms between a fluorine atom and a lithium atom.
- c) Draw a 'dot and cross' diagram to show the formation of an ionic bond between fluorine and lithium.

Q2 Potassium reacts with oxygen to form the ionic compound potassium oxide, which has the formula K_2O.

- a) Given that the oxide ion has a charge of –2, what is the charge on a potassium ion?
- b) Draw a dot-and-cross diagram to show the formation of potassium oxide from potassium and oxygen atoms.

Q3 Draw a dot-and-cross diagram to show the formation of the ionic compound sodium bromide, NaBr, from sodium and bromine atoms. Your diagram should show the outer electrons only.

Practice Questions — Fact Recall

Q1 What effect does electrostatic attraction have on oppositely charged ions?

Q2 Explain what an ionic lattice is.

Q3 Draw the structure of the sodium chloride lattice.

Q4 Explain why ionic compounds conduct electricity when molten.

Q5 Magnesium chloride is an ionic compound. Apart from the changes to its electrical conductivity when in different states, describe three physical properties you would expect magnesium chloride to have.

3. Covalent Bonding

Ionic bonding done — now it's on to covalent bonding.

Molecules

Molecules are formed when two or more atoms bond together — it doesn't matter if the atoms are the same or different. Chlorine gas (Cl_2), carbon monoxide (CO), water (H_2O) and ethanol (C_2H_5OH) are all molecules. Molecules are held together by strong **covalent bonds**. A covalent bond is the strong electrostatic attraction between a shared pair of electrons and the nuclei of the bonded atoms. Usually each of the atoms in a molecule ends up with eight electrons in its outer shell. This is good for the atoms — it's a very stable arrangement.

Dot-and-cross diagrams

Dot-and-cross diagrams can be used to show how electrons behave in covalent bonds. The bonded atoms are drawn with their outer atomic orbitals overlapping. The shared electrons that make up the covalent bond are drawn within the overlapping area. Dot-and-cross diagrams can show single or multiple covalent bonds.

Single bonds

In a single covalent bond, the atoms share one pair of electrons. In general, each atom donates one electron to the bonding pair.

Examples

Two chlorine atoms (Cl) bond covalently to form a molecule of chlorine (Cl_2) — see Figure 1. (These diagrams don't show all the electrons — just the ones in the outer shells.)

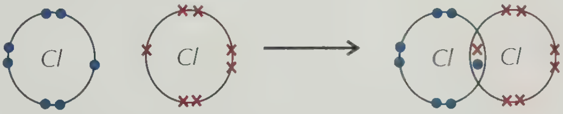


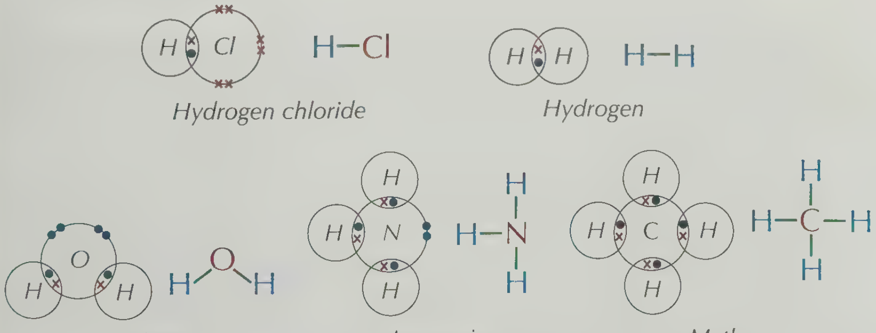
Figure 1: *Formation of a molecule of chlorine.*

A chlorine molecule can also be drawn as:

Cl—Cl

Figure 2: *Use of lines to represent covalent bonds.*

The diagrams below show other examples of covalent molecules.



Hydrogen chloride

Hydrogen

Water

Ammonia

Methane

Figure 3: *Examples of covalent molecules.*

Learning Objectives:

- Be able to define a covalent bond as the strong electrostatic attraction between a shared pair of electrons and the nuclei of the bonded atoms.
- Be able to construct 'dot-and-cross' diagrams of molecules and ions to show single covalent bonds, multiple covalent bonds and dative covalent (coordinate) bonds.
- Be able to construct 'dot-and-cross' diagrams for molecules with up to six electron pairs (including lone pairs) surrounding the central atom.
- Understand that average bond enthalpy can be used as a measurement of covalent bond strength.

Specification Reference 2.2.2

Tip: The outer electrons in hydrogen are in the first electron shell, which only needs two electrons to be filled.

Tip: Just like with dot-and-cross diagrams for ionic compounds, you can use the dots and crosses to show which atom the electrons in the bonds originally came from.

Double and triple bonds

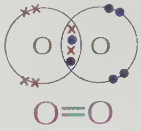
Atoms in covalent molecules don't just form single bonds — double or even triple covalent bonds can form too. In double bonds, the atoms share two pairs of electrons, and in triple bonds the atoms share three pairs of electrons.

Tip: If you count up the electrons on each atom (including the shared electrons), you'll see that they end up with eight electrons in their outer shell — this is a really stable arrangement.

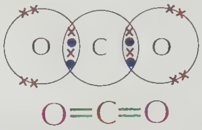
Examples

Double bonds

The oxygen atoms in O_2 are connected via a double bond. It forms because each oxygen atom has six electrons in its outer shell, so needs another two to get a full outer shell of electrons. This happens if each oxygen atom shares two electrons, forming a double bond.

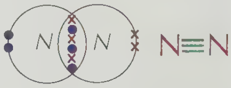


Carbon dioxide contains two C=O double bonds. Carbon has 4 electrons in its outer shell, so it needs another 4 to have a full outer shell. This means each oxygen atom must share two electrons.



Triple bonds

Nitrogen has 5 electrons in its outer shell, so it needs another 3 to have a full outer shell. The only way of doing this in N_2 is if each nitrogen atom shares three electrons, resulting in a triple bond.



Dative covalent bonding

In a normal single covalent bond, atoms share a pair of electrons — with one electron coming from each atom. In **dative covalent**, also known as **coordinate**, bonding, one of the atoms provides both of the shared electrons.

Example

The ammonium ion

The ammonium ion (NH_4^+) is formed by dative covalent bonding. It forms when the nitrogen atom in an ammonia molecule donates a pair of electrons to a proton (H^+) — see Figure 4.

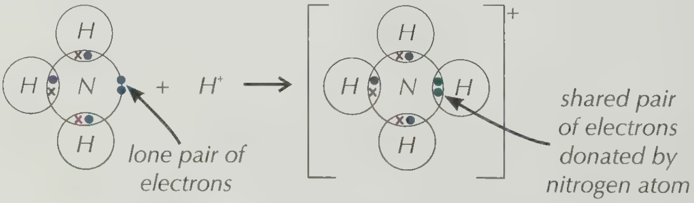


Figure 4: *Dative bonding in NH_4^+.*

Dative covalent bonding can also be shown in diagrams by an arrow, pointing away from the 'donor' atom (see Figure 5).

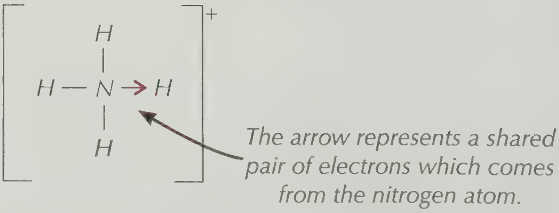

H
H — N → H
H
+
The arrow represents a shared pair of electrons which comes from the nitrogen atom.

Figure 5: *An alternative way of showing dative bonding in NH_4^+.*

Tip: Once a dative covalent bond has formed, it's no different to a normal covalent bond.

Practice Questions — Application

Q1 Draw a dot-and-cross diagram to show the bonding in the molecule chloromethane, CH_3Cl, given that the carbon atom forms four single covalent bonds. You should only show the outer electron shells.

Q2 Carbon monoxide, CO, contains a triple bond between carbon and oxygen. One of the bonds is a dative covalent bond from oxygen. Construct a dot-and-cross diagram to show the bonding in carbon monoxide. You only need to show the outer electron shells.

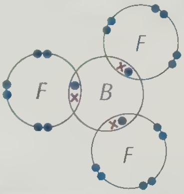
Special cases

There are always a few pesky exceptions to make life that bit trickier. For example, a few compounds contain atoms with fewer than 8 electrons in their outer shell.

Tip: Make sure you know these exceptions, and are able to draw dot-and-cross diagrams to represent their bonding.

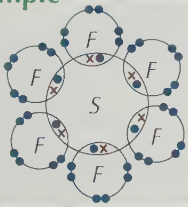
Example

In boron trifluoride, boron only has 6 electrons in its outer shell.



And a few compounds can use d-orbitals to 'expand the octet'. This means they contain atoms with more than 8 electrons in their outer shell.

Example



In sulfur hexafluoride, sulfur has 12 electrons in its outer shell.

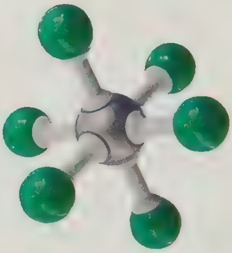


Figure 6: A molecular model of sulfur hexafluoride.

Covalent bond strength

Not all covalent bonds are the same strength — they differ depending on how much the outer atomic orbitals of the bonded atoms overlap, and how strongly the atomic nuclei are attracted to the shared electrons.

You can find out the strength of a covalent bond by looking at its **average bond enthalpy**. Average bond enthalpy measures the energy required to break a covalent bond. The stronger a bond is, the more energy is required to break it, and so the greater the value of the average bond enthalpy.

Tip: 'Enthalpy' is just a posh word for energy.

Practice Questions — Fact Recall

Q1 What is a covalent bond?

Q2 Draw a 'dot-and-cross' diagram to show the formation of a chlorine molecule.

Q3 Explain what a triple covalent bond is.

Q4 Describe the difference between a normal single covalent bond and a dative covalent bond.

Q5 Draw a 'dot-and-cross' diagram to show the bonding in BF_3.

Q6 What does the average bond enthalpy tell you about a covalent bond?

4. Shapes of Molecules

Learning Objectives:

- Know the relative repulsive strengths of bonded pairs and lone pairs of electrons.
- Be able to draw the shapes of, and state the bond angles in, molecules and ions with up to six electron pairs (including lone pairs) surrounding the central atom as predicted by electron pair repulsion.
- Be able to use electron pair repulsion to explain the following shapes of molecules and ions: linear, non-linear, trigonal planar, pyramidal, tetrahedral and octahedral.

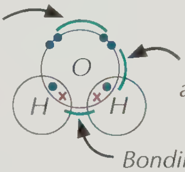
Specification Reference 2.2.2

There's a lot of variation in molecular shape and you need to understand how to work out the shape of any molecule or molecular ion. Don't worry though, the next few pages have lots of advice to help you along.

Electron pair repulsion

Molecules and molecular ions come in loads of different shapes. The shape depends on the number of pairs of electrons in the outer shell of the central atom. Pairs of electrons can be shared in a covalent bond or can be unshared. Shared electrons are called bonding pairs, unshared electrons are called **lone pairs** or non-bonding pairs.

Electrons are all negatively charged, so electron pairs will repel each other as much as they can. This sounds straightforward, but the type of electron pair affects how much it repels other electron pairs. Lone pairs repel more than bonding pairs. So, the greatest angles are between lone pairs of electrons, and bond angles between bonding pairs are often reduced because they are pushed together by lone pair repulsion. This is known as '**electron pair repulsion theory**'. Figure 1 shows the electron pairs in water.



Lone pair/lone pair bond angles are the biggest.

Lone pair/bonding pair bond angles are the second biggest.

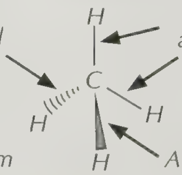
Bonding pair/bonding pair bond angles are the smallest.

***Figure 1:** Angles between electron pairs in water.*

Tip: The area where an electron pair is most likely to be found is called a 'charge cloud'. Charge clouds repel each other so that they're as far away as possible.

Drawing shapes of molecules

It can be tricky to draw molecules showing their shapes — but one way to do it is to show which way the bonds are pointing. In a molecular diagram, use wedges to show a bond pointing towards you, and a broken (or dotted) line to show a bond pointing away from you (see Figure 2).



A broken line shows a bond pointing away from you.

Lines show bonds that aren't pointing towards you or away from you.

A wedge shows a bond pointing towards you.

***Figure 2:** A molecular diagram showing the shape of methane.*

Calculating the number of electron pairs

To work out the shape of a molecule or an ion you need to know how many lone pairs and how many bonding pairs of electrons are on the central atom. Follow these steps:

1. Find the central atom — it's the one all the other atoms are bonded to.
2. Work out how many electrons are in the outer shell of the central atom. Use the periodic table to do this.
3. The formula of the molecule or ion will tell you how many atoms are bonded to the central atom so you can work out the number of electrons donated to the central atom by other atoms.

Tip: Unless one of the bonds is a dative covalent bond, each single bond to the central atom donates one electron, each double bond donates two electrons and each triple bond donates three electrons.

4. Add up the electrons and divide by 2 to find the number of electron pairs surrounding the central atom. If you're dealing with an ion, you need to take into account its charge, as it will affect the number of electrons involved in the bonding.
5. Compare the number of electron pairs to the number of bonds to find the number of lone pairs and the number of bonding pairs.

Tip: Double bonds count as two bonds, and triple bonds count as three bonds.

Examples

Carbon tetrafluoride, CF_4

1. The central atom in this molecule is carbon.
2. Carbon's in Group 4 — so it has four electrons in its outer shell.
3. There are four covalent bonds bonding the central atom to fluorine atoms, so there are four electrons coming from the fluorine atoms.
4. There are 8 electrons in total, so there are 4 electron pairs.
5. 4 pairs of electrons are involved in bonding the fluorine atoms to the carbon so there must be four bonding pairs of electrons. That accounts for all the electrons — there are no lone pairs (see Figure 3).

Tip: Elements that are in Group 7 (e.g. fluorine) can form one covalent bond with another atom to complete their outer shell. See pages 113-115 for more on covalent bonding.

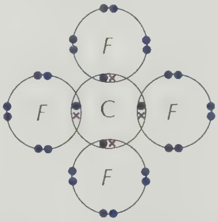


Figure 3: *A molecule of CF_4.*

Phosphorus trihydride, PH_3

1. The central atom in this molecule is phosphorus.
2. It's in Group 5 — so it has five electrons in its outer shell.
3. Phosphorus forms three covalent bonds with hydrogen, so there are three electrons coming from the hydrogen atoms.
4. There are 8 electrons in total which means 4 electron pairs.
5. Three electron pairs are involved in bonding with the hydrogen atoms (bonding pairs) and so there's one lone pair of electrons (see Figure 4).

Tip: The number of bonds the central atom forms is also called its coordination number.

Tip: A hydrogen atom will form one covalent bond with another atom to complete its outer shell.

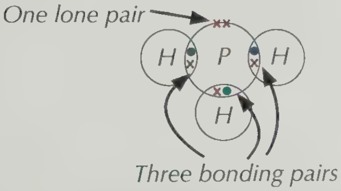


Figure 4: *Electron pairs in a molecule of PH_3.*

Working out the shapes of molecules

HOW SCIENCE WORKS

Once you know how many electron pairs are on the central atom, you can work out the shape of the molecule.

Central atoms with two electron pairs

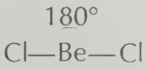
Molecules with two electron pairs have a bond angle of 180° and have a **linear** shape. This is because the pairs of bonding electrons repel each other, so they are positioned as far away from each other as possible.

Tip: You need to know how to calculate the number of electron pairs before you try and learn this bit. Make sure you've got that sorted before you go any further.

Examples — **Maths Skills**

Beryllium chloride, $BeCl_2$

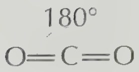
Beryllium has two bonding pairs of electrons and no lone pairs so the bond angle in $BeCl_2$ is 180° and it has a linear shape.



Tip: If the central atom forms multiple bonds, then treat each multiple bond as a single electron pair when you're working out the shape. So even though the carbon atom in carbon dioxide is surrounded by four electron pairs, the two double bonds mean that its shape is the same as for a molecule that has two electron pairs surrounding the central atom.

Carbon dioxide, CO_2

Carbon has four bonding pairs of electrons (found in two carbon-oxygen double bonds). You treat the double bonds like single bonds so CO_2 will have a linear shape.



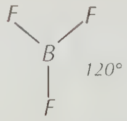
Central atoms with three electron pairs

Molecules that have three electron pairs around the central atom don't always have the same shape — the shape depends on the combination of bonding pairs and lone pairs of electrons. If there are three bonding pairs of electrons the repulsion of the charge clouds is the same between each pair and so the bond angles are all 120°. The shape of the molecule is **trigonal planar**.

Example — **Maths Skills**

Boron trifluoride, BF_3

The central boron atom has three bonding pairs of electrons, so the bond angle in BF_3 is 120° and it has a trigonal planar shape.



Exam Tip
You'll be expected to know all of the bond angles for the shapes of molecules in your exam — so make sure you learn them.

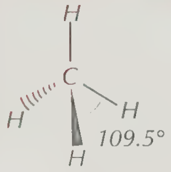
If there are two bonding pairs of electrons and one lone pair in a molecule you'll get a squished trigonal planar shape which is called **non-linear**. The bond angle will be a bit less than 120°.

Central atoms with four electron pairs

If there are four pairs of bonding electrons and no lone pairs on a central atom, all the bond angles are 109.5° — the charge clouds all repel each other equally. The shape of the molecule is **tetrahedral**.

Tip: It might help you to think of wedges as bonds that stick out of the page, broken lines as bonds that point behind the page and straight lines as bonds that are flat against the page.

Example — **Maths Skills**

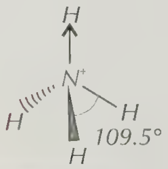


Methane, CH_4

The carbon atom has four bonding pairs of electrons so the shape of CH_4 is tetrahedral.

Ammonium ion, NH_4^+

The nitrogen atom has four bonding pairs of electrons so the shape of NH_4^+ is tetrahedral.



If there are three bonding pairs of electrons and one lone pair, the lone-pair/bonding-pair repulsion will be greater than the bonding-pair/bonding-pair repulsion and so the angles between the atoms will change. There'll be smaller bond angles between the bonding pairs of electrons and larger angles between the lone pair and the bonding pairs. The bond angle is 107° and the shape of the molecule is **trigonal pyramidal**.

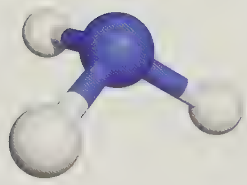
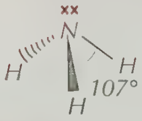


Figure 5: A molecular model of ammonia, showing it to be a trigonal pyramidal shape.

Example — **Maths Skills**

Ammonia, NH_3

The nitrogen has three bonding pairs of electrons and a lone pair, so the shape of NH_3 is trigonal pyramidal.



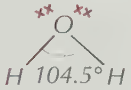
If there are two bonding pairs of electrons and two lone pairs of electrons the lone-pair/lone-pair repulsion will squish the bond angle even further. The bond angle is 104.5° and the shape of the molecules is **non-linear**.

Tip: Take a look back at the electron pair repulsion theory (page 116) for why more lone pairs means smaller bond angles.

Example — Maths Skills

Water, H_2O

The oxygen atom has two bonding pairs shared with hydrogen atoms and two lone pairs, so the shape of H_2O is non-linear (bent).



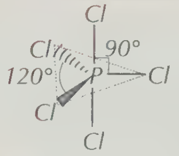
Central atoms with five or six electron pairs

Some central atoms can use d orbitals and can 'expand the octet' — which means they can have more than eight bonding electrons. A molecule with five bonding pairs will be **trigonal bipyramidal**. Repulsion between the bonding pairs means that three of the atoms will form a trigonal planar shape with bond angles of 120° and the other two atoms will be at 90° to them.

Example — Maths Skills

Phosphorus pentachloride, PCl_5

The phosphorus atom has five bonding pairs so it has a trigonal bipyramidal shape.



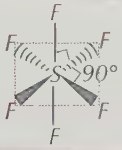
Exam Tip
You could be asked to name the shape of a molecule so learn the different names — some of the names are quite similar so make sure you spell them correctly.

A molecule with six bonding pairs will be **octahedral**. All of the bond angles in the molecule are 90°.

Example — Maths Skills

Sulfur hexafluoride, SF_6

Sulfur has six bonding pairs making its shape **octahedral**.



Practice Questions — Application

Q1 a) How many electron pairs are on the central atom of an H_2S molecule?

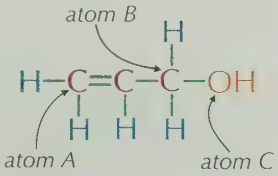
b) How many lone pairs does a molecule of H_2S have?

c) Draw and name the shape of an H_2S molecule.

d) Suggest the bond angle between bonding pairs in H_2S.

Q2 Draw and name the shape of a molecule of CCl_2F_2. Explain your answer.

Q3 Predict the shape and relevant bond angles of the bonds surrounding each of the labelled atoms in the molecule on the right:



Exam Tip
In the exam you could be asked to draw the shape of a molecule you've never met before. Don't panic, just take it step by step. Work out how many electron pairs the molecule has, then work out how many of those are lone pairs. Decide what the bond angles are in the molecule, then draw the molecule and make sure you label it neatly.

Practice Questions — Fact Recall

Q1 What is the bond angle between electron pairs in a trigonal planar molecule?

Q2 Name the structure that a molecule will have if it has six bonding pairs on the central atoms.

5. Polarisation

Learning Objectives:

- Know that electronegativity is the ability of an atom to attract the bonding electrons in a covalent bond.
- Be able to interpret Pauling electronegativity values.
- Understand that polar bonds have a permanent dipole due to the covalently-bonded atoms having different electronegativities.
- Be able to explain whether a molecule is polar based on its shape and any permanent dipoles it contains.

Specification Reference 2.2.2

Polarisation of bonds occurs because of the nature of different atomic nuclei — some are just more attractive than others.

Electronegativity

Very few compounds come even close to being purely ionic. Similarly, only bonds between atoms of a single element, like diatomic gases such as hydrogen (H_2) or oxygen (O_2), can be purely covalent. In reality, most compounds come somewhere in between the two extremes — meaning they've often got ionic and covalent properties, e.g. covalent hydrogen chloride gas molecules dissolve to form hydrochloric acid, which is an ionic solution.

Whether a bond has more covalent or ionic character depends on the difference in **electronegativity** between the bonded atoms. Electronegativity is just the ability of an atom to attract the bonding electrons in a covalent bond. Electronegativity is measured on the Pauling Scale. A higher number means an element is better able to attract the bonding electrons. Ignoring the noble gases and hydrogen, electronegativity tends to increase across periods and decrease down groups. This means that fluorine is the most electronegative element (see Figure 1). Oxygen, nitrogen and chlorine are also very strongly electronegative — see Figure 2.

Element	*Electronegativity (Pauling Scale)*
H	*2.20*
C	*2.55*
N	*3.04*
Cl	*3.16*
O	*3.44*
F	*3.98*

Figure 2: *The electronegativity of different elements.*

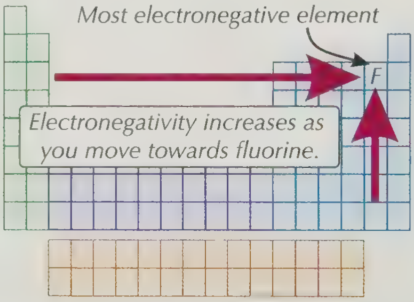

Most electronegative element
F
Electronegativity increases as you move towards fluorine.

Figure 1: *Trends of increasing electronegativity in the periodic table*

Exam Tip

You don't need to learn the electronegativity values — if you need them you'll be given them in the exam.

Polar and non-polar bonds

The covalent bonds in diatomic gases (e.g. H_2, Cl_2) are **non-polar** because the atoms have equal electronegativities and so the electrons are equally attracted to both nuclei (see Figure 3). Some elements, like carbon and hydrogen, have pretty similar electronegativities, so bonds between them are essentially non-polar.

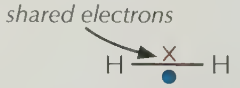

shared electrons
H
H

Figure 3: *A non-polar covalent bond in a hydrogen molecule.*

In a covalent bond between two atoms of different electronegativities, the bonding electrons are pulled towards the more electronegative atom. This makes the bond **polar** (see Figure 4).

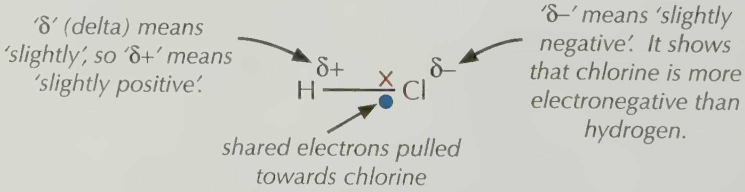

'δ' (delta) means 'slightly', so 'δ+' means 'slightly positive'.
δ+
H
Cl
δ–
'δ–' means 'slightly negative'. It shows that chlorine is more electronegative than hydrogen.
shared electrons pulled towards chlorine

Figure 4: *A polar covalent bond in a hydrogen chloride molecule.*

In a polar bond, the difference in electronegativity between the two atoms causes a **permanent dipole**. A dipole is a difference in charge between the two atoms caused by a shift in electron density in the bond. So what you need to remember is that the greater the difference in electronegativity, the more polar the bond.

Tip: It's really, really important that you get your head around the relationship between electronegativity, polarisation and dipoles. Differences in the electronegativity of atoms cause bonds to become polarised, which results in a dipole — a difference in charge between the two atoms.

Polar molecules

Polar molecules have an **overall dipole**. The arrangement of polar bonds in a molecule determines whether or not the molecule will have an overall dipole.

In simple molecules, such as hydrogen chloride, the one polar bond causes a single permanent dipole, which gives the whole molecule an overall dipole (see Figure 5).

This arrow means there's an overall dipole. It points from the positive to the negative end of the molecule.

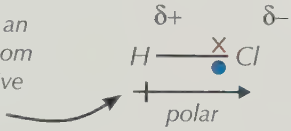


Figure 5: *Overall dipole in a molecule of hydrogen chloride.*

More complicated molecules might have several polar bonds. The shape of the molecule will decide whether or not it has an overall dipole and so whether or not it will be polar. If the polar bonds are arranged symmetrically so that the dipoles cancel each other out, such as in carbon dioxide, then the molecule has no overall dipole and is non-polar — see Figure 6.

The two polar C=O bonds exactly cancel each other out, so the molecule has no overall dipole.

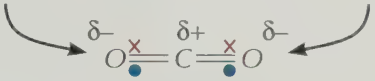


Figure 6: *A molecule of carbon dioxide has no overall dipole.*

If the polar bonds are arranged so that they all point in roughly the same direction, they won't cancel each other out and the charge will be arranged unevenly across the whole molecule. The molecule will have an overall dipole and so it will be polar.

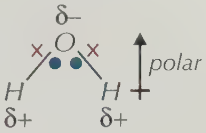


Figure 7: *The overall dipole in a molecule of water.*

Predicting bond types

HOW SCIENCE WORKS

Bonds between atoms of different elements are rarely purely ionic or purely covalent. Instead, there's a gradual transition from ionic to covalent bonding, and you can use the differences in electronegativities between two elements to predict the type of bonds that will form between them — the greater the difference, the less covalent and more ionic the bond will be. In general, bonds where the electronegativity difference between the two atoms is less than about 0.4 will be non-polar covalent bonds. If the electronegativity difference is between about 0.4 and 2.0, then the bonds will be polar but still mainly covalent in character. If the difference in electronegativity values for the two elements in the bond is more than 2.0 then the bonding will be mainly ionic in character.

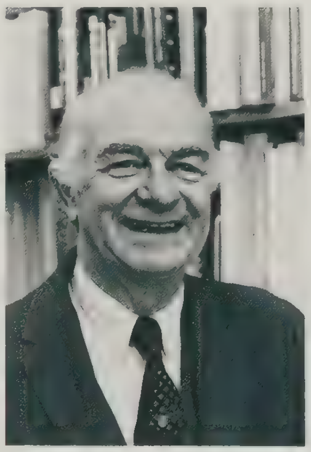


Figure 8: *Linus Pauling was the chemist who came up with the concept of electronegativity. In 1954 he was awarded the Nobel Prize for Chemistry for this work, as well as his other research into the properties of chemical bonds.*

Tip: Looking at electronegativity differences isn't a foolproof way of working out the type of bonding in a compound but it's useful for getting a rough idea of what's likely to be happening.

Examples

Oxygen has a Pauling electronegativity value of 3.44. It can form non-polar covalent, polar covalent or ionic bonds depending upon the element it is bonded to. For example:

With nitrogen:
Nitrogen has a Pauling electronegativity value of 3.04. The difference in electronegativity values is 0.4, so the nitrogen-oxygen bond in nitrogen monoxide (NO) is likely to be covalent, and either non-polar or only very slightly polar.

With hydrogen:
Hydrogen has a Pauling electronegativity value of 2.20. The difference in electronegativity values is 1.24, so the hydrogen-oxygen bonds in water (H_2O) are likely to be covalent, but quite polar in character.

With magnesium:
Magnesium has a Pauling electronegativity value of 1.31. The difference in electronegativity is 2.13, so the magnesium-oxygen bonds in magnesium oxide (MgO) are mainly ionic in character.

Element	*Electronegativity (Pauling Scale)*
B	*2.04*
P	*2.19*
H	*2.20*
C	*2.55*
N	*3.04*
Cl	*3.16*
O	*3.44*
F	*3.98*

Figure 9:
The electronegativity of different elements.

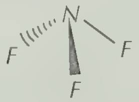
Practice Questions — Application

You may need to use Figure 9 when answering the following questions.

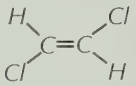
Q1 Predict whether or not the following bonds have a permanent dipole:
- a) C–O
- b) N–Cl
- c) B–F

Q2 Copy out the diagrams of the following molecules and mark any permanent dipoles on the atoms. Use this to predict whether or not the molecules are polar.

a) Nitrogen trifluoride:



b) E-dichloroethene:



Tip: Have a look back at pages 116-119 to find the rules for drawing the shapes of molecules.

Q3 Draw the shapes of the following molecules, and predict whether or not they are polar:
- a) BCl_3
- b) CH_2Cl_2
- c) PF_3

Practice Questions — Fact Recall

Q1 Chlorine is more electronegative than hydrogen. Explain what this means.

Q2 Explain why the H–F bond is polarised.

Q3 What is a dipole?

6. Intermolecular Forces

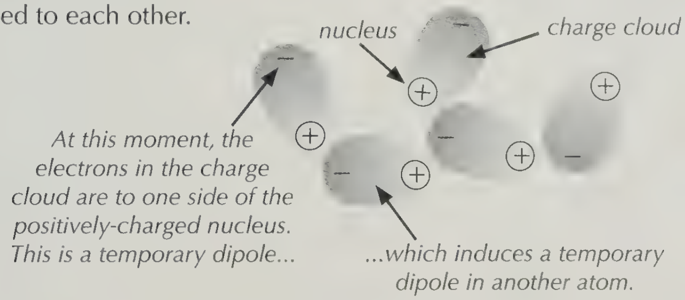
Molecules don't just exist independently — they can interact with each other. And you need to know how they interact.

What are intermolecular forces?

Intermolecular forces are forces between molecules. They're much weaker than covalent, ionic or metallic bonds. There are three types you need to know about: induced dipole-dipole interactions, permanent dipole-dipole interactions and hydrogen bonding (this is the strongest type).

Induced dipole-dipole interactions

Induced dipole-dipole interactions cause all atoms and molecules to be attracted to each other. Electrons in charge clouds are always moving really quickly. At any particular moment, the electrons in an atom are likely to be more to one side than the other. At this moment, the atom would have a temporary dipole. This dipole can cause another temporary (induced) dipole in the opposite direction on a neighbouring atom (see Figure 1). The two dipoles are then attracted to each other. The second dipole can cause yet another dipole in a third atom. It's a domino effect. Because the electrons are constantly moving, the dipoles are being created and destroyed all the time. Even though the dipoles keep changing, the overall effect is for the atoms to be attracted to each other.



At this moment, the electrons in the charge cloud are to one side of the positively-charged nucleus. This is a temporary dipole...

...which induces a temporary dipole in another atom.

Figure 1: *Temporary dipoles in a liquid resulting in induced dipole-dipole interactions.*

Example

Induced dipole-dipole interactions are responsible for holding iodine molecules together in a lattice. Iodine atoms are held together in pairs by strong covalent bonds to form molecules of I_2 (see Figure 2). But the molecules are then held together in a simple molecular lattice arrangement by induced dipole-dipole interactions (see Figure 3).

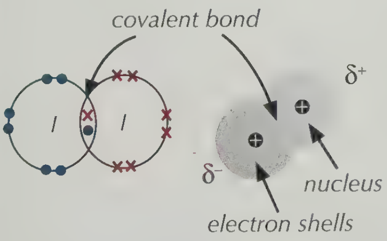


Figure 2: *A dot-and-cross diagram and a diagram showing electron density in a molecule of iodine.*

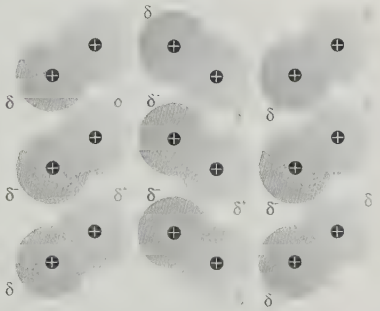


Figure 3: *Lattice of iodine molecules held together by induced dipole-dipole interactions.*

Learning Objectives:

- Understand how intermolecular forces are based on induced dipole-dipole interactions and permanent dipole-dipole interactions.
- Explain the solid structures of simple molecular lattices as covalently bonded molecules attracted by intermolecular forces, e.g. I_2 or ice.
- Understand that hydrogen bonding is intermolecular bonding between molecules containing N, O or F and the H atom of -NH, -OH or HF.
- Explain the anomalous properties of H_2O, such as its relatively high melting and boiling points and the low density of ice compared to water, as resulting from hydrogen bonding.
- Explain the effect of structure and bonding on the physical properties of covalent compounds with simple molecular lattice structures including melting and boiling points, solubility and electrical conductivity.

Specification Reference 2.2.2

Tip: Induced dipole-dipole interactions can also be called induced dipole-dipole forces.

Figure 4: *The adhesive ability of a gecko's foot is thought to be due to induced dipole-dipole interactions.*

Tip: Induced dipole-dipole interactions can also be called London (dispersion) forces.

Tip: Remember — there are induced dipole-dipole interactions between all atoms and molecules.

Exam Tip
When you're drawing dipoles in the exam, make sure you include the δ+ and δ– symbols to show the charges.

Tip: Using the electrostatic attraction between pairs of dipoles to explain the intermolecular forces in an entire substance is a great example of how science works.

HOW SCIENCE WORKS

Not all induced dipole-dipole interactions are the same strength — larger molecules have larger electron clouds, meaning stronger induced dipole-dipole interactions. Molecules with greater surface areas also have stronger induced dipole-dipole interactions because they have a more exposed electron cloud.

When you boil a liquid, you need to overcome the intermolecular forces, so that the particles can escape from the liquid surface. It stands to reason that you need more energy to overcome stronger intermolecular forces, so liquids with stronger induced dipole-dipole interactions will have higher boiling points. Induced dipole-dipole interactions affect other physical properties, such as melting point and viscosity too.

Example

Induced dipole-dipole interactions are the only forces between noble gas atoms, so the boiling points of the gases depend on them. As you go down the group of noble gases, the number of electrons increases and the atomic size also increases. This means larger temporary dipoles are able to form, so the induced dipole-dipole interactions between particles increase in strength and therefore the boiling points increase (see Figure 5).

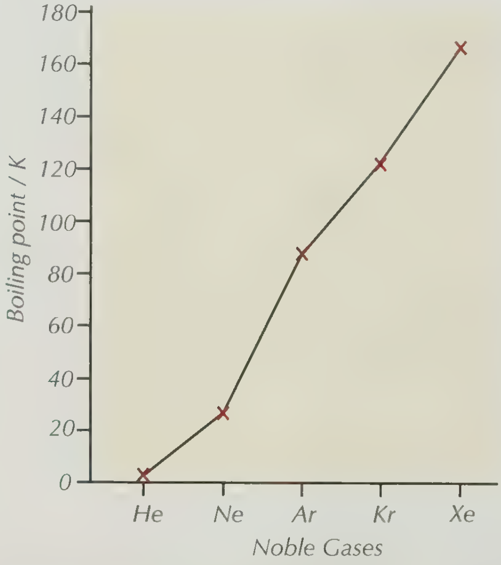


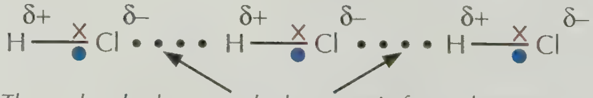
Figure 5: *Graph showing the boiling points of noble gases.*

Permanent dipole-dipole interactions

The δ+ and δ– charges on polar molecules cause weak electrostatic forces of attraction between molecules. These are called permanent dipole-dipole interactions. Permanent dipole-dipole interactions happen in addition to (not instead of) induced dipole-dipole interactions.

Example

Hydrogen chloride gas has polar molecules due to the difference in electronegativity of hydrogen and chlorine.



The molecules have weak electrostatic forces between them because of the shift in electron density.

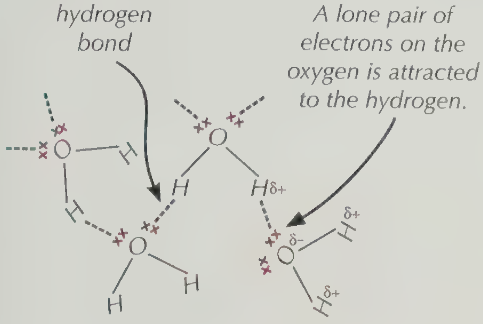
Figure 6: *Permanent dipole-dipole interactions in hydrogen chloride gas.*

Hydrogen bonding

Hydrogen bonding only happens when hydrogen is covalently bonded to fluorine, nitrogen or oxygen. Hydrogen has a high charge density because it's so small and fluorine, nitrogen and oxygen are very electronegative. The bond is so polarised that a weak bond forms between the hydrogen of one molecule and a lone pair of electrons on the fluorine, nitrogen or oxygen in another molecule. Molecules which have hydrogen bonding usually contain -OH or -NH groups.

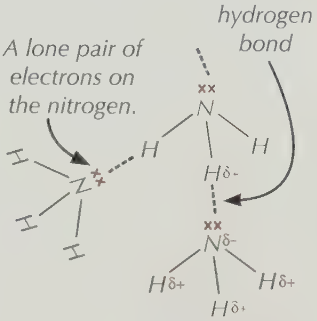
Examples

Water and ammonia both have hydrogen bonding (see Figures 7 and 8).


hydrogen bond

A lone pair of electrons on the oxygen is attracted to the hydrogen.

Figure 7: *Hydrogen bonding in water.*


A lone pair of electrons on the nitrogen.

hydrogen bond

Figure 8: *Hydrogen bonding in ammonia.*

Hydrogen bonding has a huge effect on the properties of substances. They are soluble in water and have higher boiling and melting points than molecules of a similar size that are unable to form hydrogen bonds. Water and ammonia have very high boiling points if you compare them with other hydrides in their groups, because of the extra energy needed to break the H bonds — see Figure 9.

HOW SCIENCE WORKS

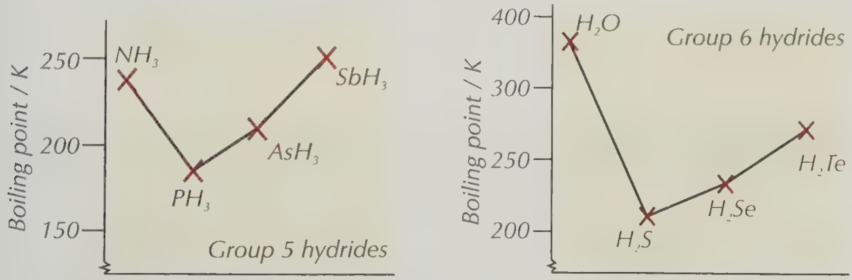


Figure 9: *Graph showing the boiling points of Group 5 and 6 hydrides.*

In ice, molecules of H_2O are held together in a lattice by hydrogen bonds — see Figure 10. When ice melts, hydrogen bonds are broken, so ice has more hydrogen bonds than liquid water. Since hydrogen bonds are relatively long, the molecules in ice will, on average, be further apart than in liquid water. This makes ice less dense than liquid water. This is unusual — most substances get denser when they freeze.

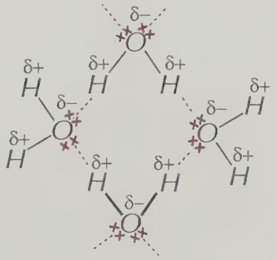


Figure 10: *Lattice of water molecules in ice held together by hydrogen bonds.*

Tip: Charge density is just a measure of how much positive or negative charge there is in a certain volume.

Exam Tip

Hydrogen bonding is a special case scenario — it only happens in specific molecules. In the exam, you could be asked to compare intermolecular forces in different substances, so you'll need to know the different intermolecular forces and their relative strengths. Don't forget that not every molecule with hydrogen in it makes hydrogen bonds.

Exam Tip

If you're asked to draw a diagram to show hydrogen bonding you'll need to include the lone pairs of electrons on the electronegative atom (O, N or F). You may also have to show the partial charges — the δ+ goes on the H atom and the δ– goes on the electronegative atom.

Exam Tip

You don't need to learn the actual boiling points of the substances in Figure 9, but you should be able to explain the shapes of the graphs.

Figure 11: *Icebergs float because ice is less dense than water.*

Tip: When you melt or boil a simple covalent compound, you just have to break the intermolecular forces that hold together the molecules in a compound. You don't have to break the covalent bonds that hold the atoms together in molecules.

Behaviour of simple covalent compounds

Simple covalent compounds have strong bonds within molecules but weak forces between the molecules. Their physical properties, such as electrical conductivity, melting point and solubility, are determined by the bonding in the compound.

Electrical conductivity

Even though some covalent molecules have permanent dipoles, overall covalent molecules are uncharged. This means they can't conduct electricity.

Melting and boiling points

The intermolecular forces that hold together the molecules in simple covalent compounds are weak so don't need much energy to break. This means their melting and boiling points are normally low — they are often liquids or gases at room temperature. As intermolecular forces get stronger, melting and boiling points increase.

Solubility

Water is a polar molecule, so only tends to dissolve other polar substances well. Compounds with hydrogen bonds, such as ammonia, can form hydrogen bonds with water molecules, so will be soluble. Molecules that aren't polar, such as methane, will be insoluble or, at best, only slightly soluble in water.

***Figure 12:** Iodine is made up of non-polar molecules, so is only slightly soluble in water. Most of the iodine crystals are undissolved at the bottom of the test tube.*

Trends in melting and boiling points

In general, the main factor that determines the boiling point of a substance will be the strength of the induced dipole-dipole forces (unless the molecule can form hydrogen bonds).

Example

As you go down the Group 7 hydrides from HCl to HI, there are two competing factors that could affect the overall strength of the intermolecular forces, and so the boiling points:

- The polarity of the molecules decreases, so the strength of the permanent dipole-dipole interactions decreases.
- The number of electrons in the molecules increases, so the strength of the induced dipole-dipole interactions increases.

As you can see from Figure 13, the boiling points of the Group 7 hydrides increase from HCl to HI. So the increasing strength of the induced dipole-dipole interactions has a greater effect on the boiling point than the decreasing strength of the permanent dipole-dipole interactions.

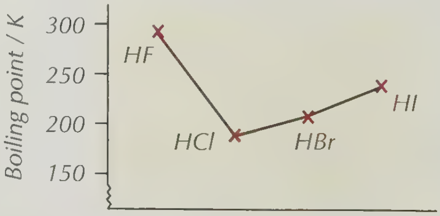


***Figure 13:** Boiling points of the Group 7 hydrides.*

Tip: The boiling points of the Group 7 hydrides are still very low — except for HF, they're all gases at room temperature.

Tip: HF has the highest boiling point of the Group 7 hydrides because it can form hydrogen bonds.

If you have two molecules with a similar number of electrons, then the strength of their induced dipole-dipole interactions will be similar. So if one of the substances has molecules that are more polar than the other, it will have stronger permanent dipole-dipole interactions and so a higher boiling point.

Practice Questions — Application

Q1 What intermolecular force(s) exist(s) in H_2?

Q2 Draw a diagram to show the intermolecular forces between three molecules of hydrogen bromide, HBr. Include bonding electrons and any partial charges in your diagram. Hydrogen has an electronegativity value of 2.20 and bromine has a value of 2.96.

Q3 The table in Figure 14 shows the electronegativity values of some elements.

a) Use the table to explain why there are hydrogen bonds between H_2O molecules but not between HCl molecules.

b) Why does water have a higher boiling point than hydrogen chloride?

c) Identify one other element from the table that would form hydrogen bonds when covalently bonded to hydrogen.

d) Name one other element from the table that would not form hydrogen bonds when covalently bonded to hydrogen.

Q4 Hydrogen has an electronegativity value of 2.20 on the Pauling scale, nitrogen has a value of 3.04 and phosphorus has a value of 2.19.

a) The boiling point of NH_3 is –33 °C and the boiling point of PH_3 is –88 °C. Explain why the boiling point of PH_3 is lower.

b) Arsenic (As) has an electronegativity value of 2.18. Would you expect the boiling point of AsH_3 to be higher or lower than that of NH_3?

Q5 Put the following compounds in order of increasing boiling point. Explain your prediction in terms of intermolecular forces:

CH_3OH, CH_4, CH_3I, CH_3Cl.

Element	*Electronegativity (Pauling Scale)*
H	*2.20*
C	*2.55*
Cl	*3.16*
O	*3.44*
F	*3.98*

Figure 14: *The electronegativity of different elements.*

Exam Tip

It's quite likely you'll be asked to identify and compare the intermolecular forces in different substances in the exam. You'll also need to know the effects that the intermolecular forces have on the properties of the substances, so make sure you know all this stuff inside out.

Practice Questions — Fact Recall

Q1 Name three types of intermolecular forces.

Q2 Describe the bonding within and between iodine molecules.

Q3 What are permanent dipole-dipole forces?

Q4 a) What is the strongest intermolecular force in ammonia?

b) Draw a diagram to show this intermolecular force between two ammonia molecules.

Q5 Explain why ice is less dense than liquid water.

Q6 Chlorine (Cl_2) is a simple covalent molecule.

a) Explain why chlorine is only slightly soluble in water.

b) Would you expect chlorine to conduct electricity? Explain your answer.

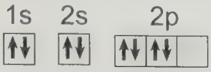
Section Summary

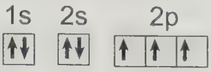
Make sure you know...

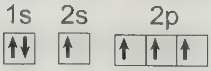
- How many electrons each of the first four shells in atoms can contain.
- How many orbitals make up the s, p and d sub-shells and how many electrons go in each of them.
- That an orbital is the bit of space that an electron moves in and that each orbital can hold up to two electrons with opposite spins.
- What shapes the s- and p-orbitals are.
- The relative energy levels of the s-, p- and d-orbitals of the first 4 electron shells.
- That electrons fill orbitals of lower energies first and that they fill orbitals with the same energy singly before they start sharing.
- How to write electron configurations using both sub-shell notation and 'electrons in boxes'.
- How to work out electron configurations of the first 36 elements from the periodic table.
- How different theories of electronic structure developed over time.
- That electrostatic attraction holds ions together and that this is called ionic bonding.
- How to draw dot-and-cross diagrams to show ionic bonding.
- That giant ionic lattices, such as sodium chloride, are regular repeating structures resulting from oppositely charged ions strongly attracted to each other in all directions.
- How the structure and bonding of ionic compounds decides their physical properties — their electrical conductivity, melting and boiling points and solubility.
- That a covalent bond is the strong electrostatic attraction between a shared pair of electrons and the nuclei of the bonded atoms.
- That dative covalent bonds form when one atom donates both the shared electrons in a bond.
- How to draw dot-and-cross diagrams to show single, multiple and dative covalent bonds between atoms, for molecules with up to six electron pairs around the central atom.
- That the larger the value of the average bond enthalpy, the stronger a covalent bond will be.
- How the repulsion between electron pairs on a central atom affects the shape of simple molecules.
- How to use electron pair repulsion theory to predict the shapes of molecules that have central atoms with 2, 3, 4, 5 and 6 electron pairs, including their bond angles and shape names.
- How to draw 3-D diagrams to illustrate the shapes of molecules and ions.
- That electronegativity is the ability to attract the bonding electrons in a covalent bond.
- That electronegativity increases towards fluorine in the periodic table.
- How differences in electronegativities between bonding atoms causes polarisation and permanent dipoles in covalent bonds.
- The difference between polar and non-polar bonds.
- How the shape of a molecule and the polarity of its bonds affects whether or not it has an overall dipole and is a polar molecule.
- How to use Pauling electronegativity values to predict the type of bond that will form between atoms.
- What permanent dipole-dipole interactions and induced dipole-dipole interactions are, and what causes them.
- That solid structures of simple molecular substances contain covalently bonded molecules attracted to each other by intermolecular forces.
- How hydrogen bonds form and their effect on the properties of compounds.
- How the structure and bonding of covalent compounds with simple molecular structures decides their physical properties — their electrical conductivity, melting and boiling points and solubility.

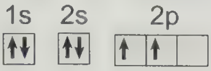
Exam-style Questions

1 Which of the options below gives the correct electron configuration for the specified atom?

A Oxygen: 

B Nitrogen: 

C Carbon: 

D Boron: 

(1 mark)

2 Which of the following statements about hydrogen selenide, H_2Se, is correct?

A Hydrogen selenide is a linear molecule.

B Hydrogen selenide has a higher boiling point that hydrogen sulfide (H_2S).

C There is one lone pair and two bonding pairs around the central Se atom in H_2Se.

D Hydrogen selenide is able to form hydrogen bonds.

(1 mark)

3 Potassium oxide, K_2O, has a melting point of 740 °C. It is an electrical insulator when it is a solid, but once molten or dissolved it can carry an electrical charge.

Silicon dioxide, SiO_2, has a melting point of 1600 °C. It is an electrical insulator and is insoluble in water.

From the table below, select the option that gives the correct structure for both compounds.

	K_2O	SiO_2
A	ionic	metallic
B	giant covalent	ionic
C	metallic	giant covalent
D	ionic	giant covalent

(1 mark)

4 Which of the following molecules does **not** have a trigonal pyramidal shape?

A H_3O^+

B NCl_3

C BCl_3

D PF_3

(1 mark)

5 The table below shows the electronegativities of some elements.

Element	C	H	Cl	O	F
Electronegativity (Pauling Scale)	2.55	2.20	3.16	3.44	3.98

(a) (i) Define the term electronegativity.

(1 mark)

(ii) Explain how electronegativity can give rise to permanent dipole-dipole interactions.

(2 marks)

(b) (i) Use the information in the table to name all the intermolecular forces in each of the following compounds:

HCl
CH_4
HF

(3 marks)

(ii) Draw a diagram to show the strongest intermolecular forces between two HF molecules. Include partial charges and all lone pairs.

(3 marks)

(iii) Explain why the only forces between Cl_2 molecules are induced dipole-dipole interactions.

(1 mark)

6 Calcium is an element that can react to form ionic bonds with negatively charged ions.

(a) Calcium can react with oxygen to form the ionic compound calcium oxide, CaO.

(i) State what is meant by the term ionic bond.

(1 mark)

(ii) Give the electronic configuration of the calcium ion, Ca^{2+}, using sub-shell notation.

(1 mark)

(iii) Draw a dot-and-cross diagram to show the bonding in CaO.
Show the outer electrons only.

(2 marks)

(b) Calcium can also form the ionic compound calcium carbonate. Calcium carbonate decomposes when heated to form calcium oxide and carbon dioxide.

State the shape and bond angle of a molecule of carbon dioxide.

Explain why carbon dioxide has this shape.

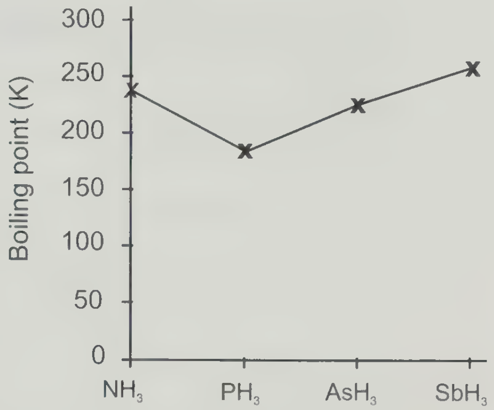
(3 marks)

(c) Predict, with reasoning, whether calcium oxide or carbon dioxide will have a higher boiling point.

(2 marks)

7 The Group 5 elements include nitrogen, phosphorus, arsenic and antimony. They can form covalent bonds with hydrogen.

(a) The graph below shows the boiling points of some Group 5 hydrides.



Explain the trend in boiling points shown by the graph for NH_3, PH_3, AsH_3 and SbH_3.

(4 marks)

(b) Draw the shape of a molecule of PH_3, labelling the size of the bond angles.

(2 marks)

(c) Explain why ammonia, NH_3, is the most soluble of the Group 5 hydrides.

(2 marks)

8 Fluorine can form covalent bonds with sulfur, S_8, to produce the molecule SF_6 and boron to form the molecule BF_3.

(a) Draw a dot-and-cross diagram to show the bonding in SF_6.
Use your diagram to explain the shape of the molecule.

(4 marks)

(b) A fluorine ion, F^-, can react with BF_3 to form the BF_4^- ion.
A dative covalent bond forms between F^- and BF_3.

(i) State the bond angle in BF_3.

(1 mark)

(ii) Explain what is meant by the term dative covalent bond.

(1 mark)

(iii) Draw a dot-and-cross diagram to show the bonding in a BF_4^- ion.
Your diagram should show the outer electrons only.

(1 mark)

(iv) Predict the shape of the BF_4^- ion. Explain your answer.

(2 marks)

Module 3 Section 1: The Periodic Table

Learning Objectives:

- Understand the development of the Periodic Law and its acceptance by the scientific community.
- Understand how the periodic table was extended through discovery and confirmation of new elements.
- Know that in the periodic table, elements are arranged by increasing atomic (proton) number.
- Know that the elements in a period show repeating trends in physical and chemical properties (periodicity).
- Know that elements in the same group have similar chemical properties.
- Understand the periodic trend in electron configurations across Periods 2 and 3.
- Know that elements are classified into s-, p- and d-blocks.

Specification Reference 3.1.1

1. The Periodic Table

You'll remember from GCSE that the periodic table isn't just arranged how it is by chance. There are well-thought-out reasons behind it, and you can use it to predict what the properties of an element might be. Read on...

Grouping the elements

HOW SCIENCE WORKS

In the early 1800s, there were only two ways to categorise elements — by their physical and chemical properties and by their **relative atomic mass**. (The modern periodic table is arranged by proton number, but back then, they knew nothing about protons or electrons. The only thing they could measure was relative atomic mass.)

In 1817, Johann Döbereiner attempted to group similar elements — these groups were called Döbereiner's triads. He saw that chlorine, bromine and iodine had similar characteristics. He also realised that other properties of bromine (e.g. atomic weight) fell halfway between those of chlorine and iodine. He found other such groups of three elements (e.g. lithium, sodium and potassium), and called them triads. It was a start.

An English chemist called John Newlands had the first good stab at making a table of the elements in 1863. He noticed that if he arranged the elements in order of mass, elements with similar chemical and physical properties appeared at regular intervals — every eighth element was similar. He called this the law of octaves, and he listed some known elements in rows of seven so that the similar elements lined up in columns — see Figure 1. The law of octaves later developed into the Periodic Law which states that if you arrange elements in order of increasing atomic number then their chemical and physical properties will repeat in a systematic way that can be predicted.

Elements arranged in rows of seven.

1	2	3	4	5	6	7
Li	*Be*	*B*	*C*	*N*	*O*	*F*
Na	*Mg*	*Al*	*Si*	*P*	*S*	*Cl*

Similar elements in columns.

Figure 1: *The arrangement of elements by John Newlands.*

The problem was, the pattern broke down on the third row, with many transition metals like Fe, Cu and Zn messing it up completely.

Mendeleev's table

HOW SCIENCE WORKS

In 1869, Russian chemist Dmitri Mendeleev produced a much better table, which wasn't far off the one we have today. He arranged all the known elements by atomic mass (like Newlands did), but the clever thing he did was to leave gaps in the table where the next element didn't seem to fit. By putting in gaps, he could keep elements with similar chemical properties in the same group — see Figure 2.

He also predicted the properties of undiscovered elements that would go in the gaps. When elements were later discovered (e.g. germanium, scandium and gallium) with properties that matched Mendeleev's predictions, it showed that clever old Mendeleev had got it right.

Tip: The discovery of the missing elements was good evidence that Mendeleev was on the right lines.

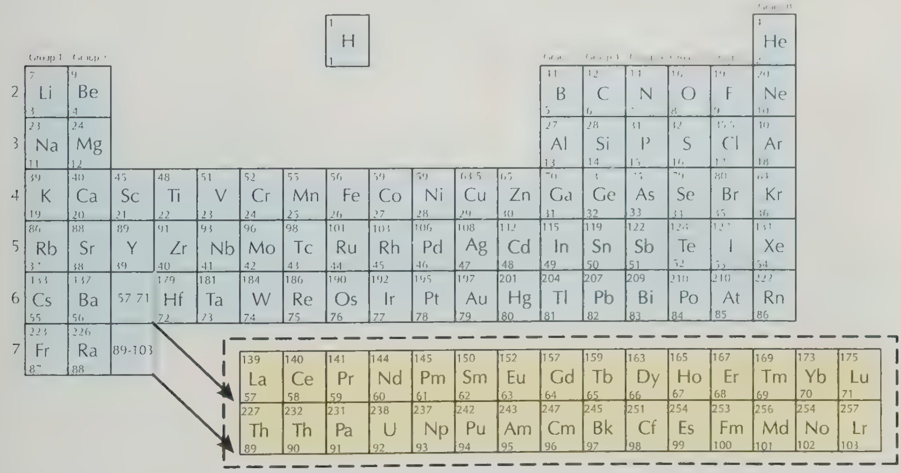
	Group 1	Group 2	Group 3	Group 4	Group 5	Group 6	Group 7
1	H						
2	Li	Be	B	C	N	O	F
3	Na	Mg	Al	Si	P	S	Cl
4	K Cu	Ca Zn	? ?	Ti ?	V As	Cr Se	Mn Br
5	Rb Ag	Sr Cd	Y In	Zr Sn	Nb Sb	Mo Te	? I
6	Cs Au	Ba Hg	La Tl	? Pb	Ta Bi	W ?	? ?

Figure 2: Dmitri Mendeleev's table of elements. The question marks show gaps in the table which were later filled when new elements were discovered.

Figure 3: Dmitri Mendeleev (1834-1907) was a Russian chemist who developed the periodic table.

The modern periodic table

The modern periodic table is pretty much the one produced by Henry Moseley around 1914. He arranged the elements according to increasing atomic number rather than by mass. This fixed a few elements that Mendeleev had put out of place using atomic mass. He also added the noble gases (Group 0) which had been discovered in the 1890s. The final big change was a result of the work of Glenn Seaborg. He suggested how the f-block elements fit into the periodic table (though they're usually shown separated from the main part of the table). The modern periodic table is shown in Figure 4.



								1 H 1										4 He 2
2	7 Li 3	9 Be 4											11 B 5	12 C 6	14 N 7	16 O 8	19 F 9	20 Ne 10
3	23 Na 11	24 Mg 12											27 Al 13	28 Si 14	31 P 15	32 S 16	35.5 Cl 17	40 Ar 18
4	39 K 19	40 Ca 20	45 Sc 21	48 Ti 22	51 V 23	52 Cr 24	55 Mn 25	56 Fe 26	59 Co 27	59 Ni 28	63.5 Cu 29	65 Zn 30	70 Ga 31	73 Ge 32	75 As 33	79 Se 34	80 Br 35	84 Kr 36
5	86 Rb 37	88 Sr 38	89 Y 39	91 Zr 40	93 Nb 41	96 Mo 42	98 Tc 43	101 Ru 44	103 Rh 45	106 Pd 46	108 Ag 47	112 Cd 48	115 In 49	119 Sn 50	122 Sb 51	128 Te 52	127 I 53	131 Xe 54
6	133 Cs 55	137 Ba 56	57 71	179 Hf 72	181 Ta 73	184 W 74	186 Re 75	190 Os 76	192 Ir 77	195 Pt 78	197 Au 79	201 Hg 80	204 Tl 81	207 Pb 82	209 Bi 83	210 Po 84	210 At 85	222 Rn 86
7	223 Fr 87	226 Ra 88	89-103															

139 La 57	140 Ce 58	141 Pr 59	144 Nd 60	145 Pm 61	150 Sm 62	152 Eu 63	157 Gd 64	159 Tb 65	163 Dy 66	165 Ho 67	167 Er 68	169 Tm 69	173 Yb 70	175 Lu 71
227 Th 89	232 Th 90	231 Pa 91	238 U 92	237 Np 93	242 Pu 94	243 Am 95	247 Cm 96	245 Bk 97	251 Cf 98	254 Es 99	253 Fm 100	256 Md 101	254 No 102	257 Lr 103

Figure 4: The modern periodic table.

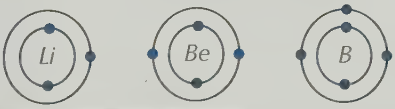
Periods and rows

The periodic table is arranged into **periods** (rows) and **groups** (columns). All the elements within a period have the same number of electron shells (if you don't worry about the sub-shells).

Example

The elements in Period 2 all have 2 electron shells:

The first three elements in Period 2.



All have two electron shells.

This results in repeating patterns of physical and chemical properties across a period (this is known as **periodicity**).

Tip: The atomic number is the number of protons in the nucleus — so it's also known as the proton number.

Exam Tip

You'll be given a periodic table in your exam, so you'll have a copy to refer to. It's a good idea to be familiar with how it works before you go into the exam though.

Tip: When you arrange elements by atomic number, there are a few that no longer go in order of atomic mass. For example, Ar would go after K if you put the elements in order of atomic mass. But Ar comes before K in the modern periodic table.

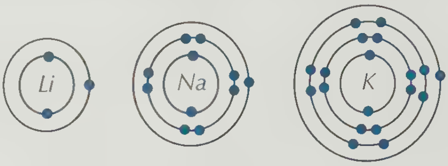
Tip: The elements of Period 1 (hydrogen and helium) both have 1 electron shell.

All the elements within a group have the same number of electrons in their outer shell. This means they have similar physical and chemical properties. The group number tells you the number of electrons in the outer shell.

Figure 5: *The Group 1 elements potassium (top left), sodium (top right) and lithium (bottom) all react strongly with water.*

Examples

Group 1 elements have 1 electron in their outer shell:



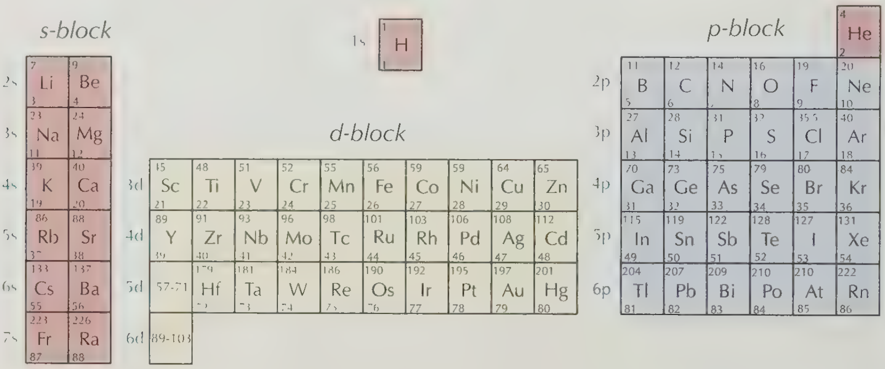
As a result the elements in Group 1 all have similar properties. For example, they all react strongly with water (see Figure 5).

Group 4 elements have 4 electrons in their outer shell and so on.

The only elements where the group number doesn't tell you how many electrons are in their outer shells are the Group 0 elements — they have full outer shells.

Electron configurations

You can use the periodic table to work out electron configurations. The period number tells you how many electron shells the element has and the group number tells you how many electrons an element has in its outer electron shell. But to make things even easier the periodic table can be split into an s-block, d-block and p-block (see Figure 6). Doing this shows you which sub-shells all the electrons go into.



	s-block			d-block											p-block					
1s	1 H 1																			4 He 2
2s	7 Li 3	9 Be 4												2p	11 B 5	12 C 6	14 N 7	16 O 8	19 F 9	20 Ne 10
3s	23 Na 11	24 Mg 12												3p	27 Al 13	28 Si 14	31 P 15	32 S 16	35.5 Cl 17	40 Ar 18
4s	39 K 19	40 Ca 20	3d	45 Sc 21	48 Ti 22	51 V 23	52 Cr 24	55 Mn 25	56 Fe 26	59 Co 27	59 Ni 28	64 Cu 29	65 Zn 30	4p	70 Ga 31	73 Ge 32	75 As 33	79 Se 34	80 Br 35	84 Kr 36
5s	86 Rb 37	88 Sr 38	4d	89 Y 39	91 Zr 40	93 Nb 41	96 Mo 42	98 Tc 43	101 Ru 44	103 Rh 45	106 Pd 46	108 Ag 47	112 Cd 48	5p	115 In 49	119 Sn 50	122 Sb 51	128 Te 52	127 I 53	131 Xe 54
6s	133 Cs 55	137 Ba 56	5d	57-71	179 Hf 72	181 Ta 73	184 W 74	186 Re 75	190 Os 76	192 Ir 77	195 Pt 78	197 Au 79	201 Hg 80	6p	204 Tl 81	207 Pb 82	209 Bi 83	210 Po 84	210 At 85	222 Rn 86
7s	223 Fr 87	226 Ra 88	6d	89-103																

Figure 6: *The periodic table showing the s-block, p-block and d-block.*

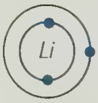
Exam Tip
You won't get a periodic table split up like this in the exam so you need to remember what the different blocks are.

s-block elements

The s-block elements have an outer shell electron configuration of s^1 or s^2.

Examples

Lithium is in Group 1 and Period 2:

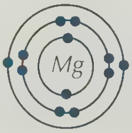


group number

Its electron configuration is: $1s^2\ \mathbf{2s^1}$

period number

Magnesium is in Group 2 and Period 3:



Its electron configuration is: $1s^2\ 2s^2\ 2p^6\ \mathbf{3s^2}$

period number group number

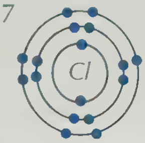
Tip: If you can't remember what sub-shells are, don't know what the electron configuration of an element shows, or can't quite get your head around what all this $1s^2\ 2s^2\ 2p^6$ business is, then have a look back at pages 106 and 107 — it's all explained in more detail there.

p-block elements

The p-block elements have an outer shell configuration of $s^2\ p^1$ to $s^2\ p^6$.

Example

Chlorine is in Group 7 and Period 3:



Its electron configuration is:

2 + 5 = 7 = group number

$1s^2\ 2s^2\ 2p^6\ \mathbf{3s^2}\ \mathbf{3p^5}$

period number

d-block elements

The d-block elements have electron configurations in which d sub-shells are being filled. They're a bit trickier — you don't always write the sub-shells in the order they're filled. Instead, you write them in order of increasing period number.

Example

The electron configuration of cobalt is: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ \mathbf{3d^7}\ 4s^2$

Even though the 3rd sub-shell fills last in cobalt, it's not written at the end of the line.

Tip: Watch out for the fact that 3d is on the same row as 4s and 4p in the periodic table. Remember that the 4s sub-shell is of lower energy than the 3d sub-shell so it fills first. Sneaky.

Working out the electron configuration of an element

When you've got the periodic table labelled with the shells and sub-shells, it's pretty easy to read off the electron structure of any element by starting at the top and working your way across and down until you get to your element.

Example

To work out the electron structure of phosphorus (P), you can use the periodic table to see that it's in Group 5 and Period 3. Starting with Period 1, the electron configuration of a full shell is $1s^2$. For Period 2 it's $2s^2\ 2p^6$. However, phosphorus' outer shell is only partially filled — it's got 5 outer electrons in the configuration $3s^2\ 3p^3$.

So: Period 1 — $1s^2$

Period 2 — $2s^2\ 2p^6$

Period 3 — $3s^2\ 3p^3$

The full electron structure of phosphorus is: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$.

Tip: It doesn't really matter how you work out the electron configurations of elements, whether you use the rules on page 108 or whether you read them off the periodic table like on this page. The important thing is that you get them right — so find a method you're happy with and stick with it.

Practice Questions — Application

Q1 How many electron shells do atoms of the following elements have?

a) Sulfur, S b) Bromine, Br c) Rubidium, Rb

Q2 How many electrons are in the outer shell of atoms of these elements?

a) Selenium, Se b) Aluminium, Al c) Potassium, K

Q3 Work out the electron configurations of the following elements:

a) Sodium, Na b) Calcium, Ca c) Chlorine, Cl

d) Arsenic, As e) Vanadium, V f) Scandium, Sc

Tip: Don't forget that you always write the sub-shells in electron configurations in order of increasing period number, even if this isn't the order that they're filled in.

Practice Questions — Fact Recall

Q1 a) How did Mendeleev arrange the elements in his version of the periodic table?

b) How are elements arranged in the modern periodic table?

Q2 a) What is a period?

b) What is a group?

c) Define the term periodicity.

Q3 Explain why elements in a group have similar chemical properties.

2. First Ionisation Energy

Learning Objectives:

- Define the term first ionisation energy.
- Explain the trend in first ionisation energies across Periods 2 and 3, and down a group, in terms of attraction, nuclear charge and atomic radius.
- Understand how trends in ionisation energies support the Bohr model of the atom.

Specification Reference 3.1.1

More stuff on electron configurations coming up. The title may be first ionisation energy, but it's still all about electrons and how they're arranged.

Ionisation energy

When electrons have been removed from an atom or molecule, it's been ionised. The energy you need to remove the first electron is called the **first ionisation energy**.

> The first ionisation energy is the energy needed to remove 1 mole of electrons from 1 mole of gaseous atoms.

You have to put energy in to ionise an atom or molecule, so it's an endothermic process. You can write equations for this process — here's the equation for the first ionisation of oxygen:

$$O_{(g)} \rightarrow O^+_{(g)} + e^- \qquad \text{1st ionisation energy} = +1314\ \text{kJ mol}^{-1}$$

Here are a few rather important points about ionisation energies:

- You must use the gas state symbol, (g), because ionisation energies are measured for gaseous atoms.
- Always refer to 1 mole of atoms, as stated in the definition, rather than to a single atom.
- The lower the ionisation energy, the easier it is to form an ion.

Tip: An endothermic process is one that takes in heat — see page 167 for more on this.

Factors affecting ionisation energy

A high ionisation energy means there's a strong attraction between the electron and the nucleus, so more energy is needed to overcome the attraction and remove the electron. Three things can affect ionisation energy:

1. Nuclear charge

The more protons there are in the nucleus, the more positively charged the nucleus is and the stronger the attraction for the electrons.

2. Atomic radius

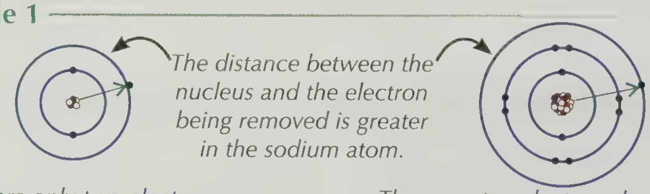
Attraction falls off very rapidly with distance. An electron close to the nucleus will be much more strongly attracted than one further away.

3. Shielding

As the number of electrons between the outer electrons and the nucleus increases, the outer electrons feel less attraction towards the nuclear charge. This lessening of the pull of the nucleus by inner shells of electrons is called shielding.

Exam Tip
Make sure you know the definition of first ionisation energy — it could come up in your exam.

Example 1



The distance between the nucleus and the electron being removed is greater in the sodium atom.

There are only two electrons between the nucleus and the outer electron in a lithium atom.

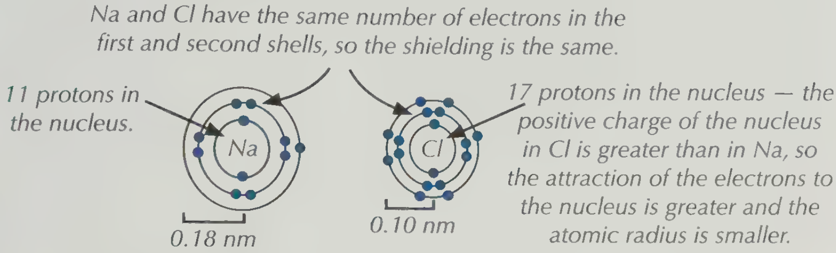
There are ten electrons between the nucleus and the outer electron in a sodium atom — the shielding effect is greater.

Figure 1: *A lithium atom and a sodium atom.*

This means that lithium has a higher first ionisation energy (519 kJ mol^{-1}) than sodium (496 kJ mol^{-1}). (The shielding and the atomic radius have a bigger effect than the nuclear charge in this example.)

Example 2

As the number of protons increases, the positive charge of the nucleus increases. This means electrons are pulled closer to the nucleus, making the atomic radius smaller.



Na and Cl have the same number of electrons in the first and second shells, so the shielding is the same.
11 protons in the nucleus.
Na
Cl
17 protons in the nucleus — the positive charge of the nucleus in Cl is greater than in Na, so the attraction of the electrons to the nucleus is greater and the atomic radius is smaller.
0.18 nm
0.10 nm

Figure 2: *A sodium atom and a chlorine atom.*

This means that chlorine has a higher first ionisation energy (1256 kJ mol^{-1}) than sodium (496 kJ mol^{-1}). (The nuclear charge and the atomic radius determine this, as the shielding is the same.)

Tip: You can only really see the effect of nuclear charge on ionisation energy if you're looking at atoms with equal shielding effects. This only really happens when you're looking at elements in the same period of the Periodic Table.

Figure 3: *Cut sodium metal.*

Trend in ionisation energy down a group

As you go down a group in the periodic table, ionisation energies generally fall, i.e. it gets easier to remove outer electrons (see Figure 4).

This is because elements further down a group have extra electron shells compared to ones above. The extra shells mean that the atomic radius is larger, which greatly reduces the attraction to the nucleus. The extra inner shells also shield the outer electrons from the attraction of the nucleus. Both of these factors make it easier to remove outer electrons, resulting in a lower ionisation energy. The positive charge of the nucleus does increase as you go down a group (due to the extra protons), but this effect is overridden by the effect of the extra shells.

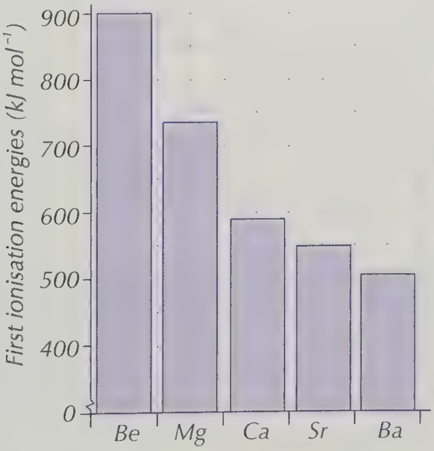


Figure 4: *First ionisation energies of the first five elements of Group 2.*

Exam Tip

If you're asked about trends in ionisation energy in a group or across a period, you can work them out by thinking about how the three factors that affect ionisation energy (atomic radius, nuclear charge and shielding) change.

Tip: Periodicity is the repeating trends in physical and chemical properties of elements as you go across a period.

Periodicity of ionisation energy

As you move across a period, the general trend is for the ionisation energies to increase — i.e. it gets harder to remove the outer electrons. This is because the number of protons is increasing, which means a higher nuclear charge, so a smaller atomic radius and a stronger attraction. All the extra electrons are at roughly the same energy level, even if the outer electrons are in different orbital types. This means there's generally little extra shielding effect to lessen the attraction from the nucleus.

Examples

In Period 2 the first ionisation energies generally increase from lithium to neon and in Period 3 the first ionisation energies generally increase from sodium to argon (see Figure 5).

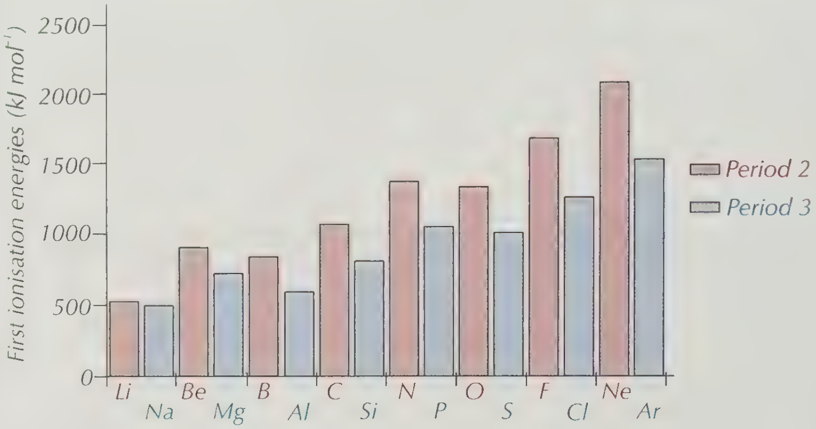


Figure 5: *The trend in first ionisation energies across Periods 2 and 3.*

As you go across Period 2 or Period 3, the number of protons in the nucleus increases. This means the overall attraction between the electrons and the nucleus increases, the atomic radius decreases and the outer electrons get more difficult to remove.

Exam Tip
There's no need to memorise the graphs in this section, but you do need to know their shapes and be able to explain them.

You might have spotted that in Figure 5, the ionisation energies across a period don't always increase — there are small drops between Groups 2 and 3, and 5 and 6.

The drop between Groups 2 and 3 is due to the outer electrons in Group 3 elements being in a p-orbital rather than an s-orbital.

Example

Mg	$1s^2\ 2s^2\ 2p^6\ 3s^2$	1st ionisation energy = 738 kJ mol^{-1}
Al	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$	1st ionisation energy = 578 kJ mol^{-1}

- Aluminium's outer electron is in a 3p orbital rather than a 3s. The 3p orbital has a slightly higher energy than the 3s orbital, so the electron is, on average, to be found further from the nucleus.
- The 3p orbital also has additional shielding provided by the $3s^2$ electrons.

Both these factors together are strong enough to override the effect of the increased nuclear charge, resulting in the ionisation energy dropping slightly. This pattern in ionisation energies provides evidence for the theory of electron sub-shells.

Tip: This is an example of how real-life data (the first ionisation energies of atoms) can provide evidence for a theory (Bohr's model of the atom). See page 43 for more.

HOW SCIENCE WORKS

The drop between Groups 5 and 6 is due to electron repulsion.

Example

Phosphorus: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$ 1st ionisation energy = 1012 kJ mol^{-1}

Sulfur: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$ 1st ionisation energy = 1000 kJ mol^{-1}

The shielding is identical in the phosphorus and sulfur atoms, and in both cases the electron is being removed from an orbital in the 3p sub-shell.

In phosphorus's case, the electron is being removed from a singly-occupied orbital. But in sulfur, the electron is being removed from an orbital containing two electrons.

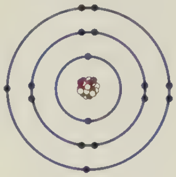
Phosphorus: *[Ne]* $\overset{3s}{\boxed{\uparrow\downarrow}}\ \overset{3p}{\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}}$ *Sulfur*: *[Ne]* $\overset{3s}{\boxed{\uparrow\downarrow}}\ \overset{3p}{\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow}}$

The repulsion between two electrons in an orbital means that electrons are easier to remove from shared orbitals. Yup, yet more evidence for the electronic structure model.

Tip: Writing out or drawing the electronic configurations of elements can help you work out why their ionisation energies are what they are.
For example, drawing

$\boxed{\uparrow\downarrow}\ \boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow}$

will show you that the electron being removed is paired, so there will be repulsion. Drawing



will show you how much shielding there is.

Practice Questions — Application

Q1 a) Write an equation for the first ionisation energy of chlorine.

b) Write an equation for the first ionisation energy of silicon.

Q2 a) Explain why the atomic radius of aluminium is larger than the atomic radius of sulfur.

b) Name a Period 3 element with a larger atomic radius than aluminium.

Q3 The first ionisation energy of aluminium is 578 kJ mol^{-1}. The first ionisation energy of silicon is 787 kJ mol^{-1}. Explain why there is a difference between these ionisation energies.

Q4 a) Would you expect strontium to have a larger or smaller atomic radius than rubidium? Explain your answer.

b) Would you expect bromine to have a higher or lower first ionisation energy than selenium? Explain your answer.

Q5 The first ionisation energy of nitrogen is 1402 kJ mol^{-1}. The first ionisation energy of oxygen is 1314 kJ mol^{-1}. Explain why there is a difference between these ionisation energies.

Q6 The first ionisation energy of beryllium is 900 kJ mol^{-1}. The first ionisation energy of boron is 801 kJ mol^{-1}. Explain why there is a difference between these ionisation energies.

Exam Tip
If you get a question in the exam asking you to compare ionisation energies, make sure you remember the 3 factors that affect ionisation energy. Work out how the factors differ between each element, and you should have a very good idea of your answer.

Practice Questions — Fact Recall

Q1 Define first ionisation energy.

Q2 How does the number of protons affect the first ionisation energy?

Q3 Give two other factors that affect the first ionisation energy.

Q4 Explain why first ionisation energies decrease down a group.

Q5 a) Describe the general trend in ionisation energy across a period of the periodic table.

b) Explain this trend.

Exam Tip
If you're asked about a specific trend, it might help you to roughly sketch out the shape of the relevant graph. That way you'll easily be able to see how the values for the elements compare to each other.

3. Successive Ionisation Energies

Learning Objectives:

- Understand the term successive ionisation energy.
- Predict from successive ionisation energies the number of electrons in each shell of an atom, and the group of the element.

Specification Reference 3.1.1

First ionisation energy is the energy needed to remove 1 mole of electrons from 1 mole of gaseous atoms. You'll now see second, third and all other ionisation energies, collectively known as successive ionisation energies.

What are successive ionisation energies?

You can remove all the electrons from an atom, leaving only the nucleus. Each time you remove an electron, there's a **successive ionisation energy**. These are called second ionisation energy, third ionisation energy... and so on. For example, the **second ionisation energy** is the energy needed to remove 1 electron from each ion in 1 mole of gaseous 1+ ions to form 1 mole of gaseous 2+ ions.

Here's the equation for the second ionisation of oxygen :

$$O^{+}_{(g)} \rightarrow O^{2+}_{(g)} + e^{-} \qquad \text{2nd ionisation energy} = +3388\ \text{kJ mol}^{-1}$$

Ionisation energies and shell structure

If you have the successive ionisation energies of an element you can work out the number of electrons in each shell of the atom and which element the group is in. A graph of successive ionisation energies provides evidence for the shell structure of atoms (see Figure 1).

HOW SCIENCE WORKS

Tip: The y-axis of this graph has a log (logarithmic) scale. Log scales go up in powers of a number (e.g. 1, 10, 100, etc.) rather than in units (1, 2, 3, etc.). Log scales are often used for graphs like this because ionisation energy values have such a huge range.

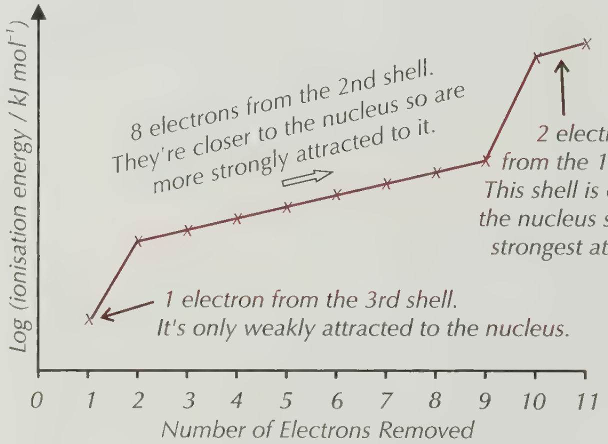


Figure 1: *Successive ionisation energies of sodium.*

Within each shell, successive ionisation energies increase. This is because electrons are being removed from an increasingly positive ion — there's less repulsion amongst the remaining electrons, so more energy is needed to remove the next electron. The big jumps in ionisation energy happen when a new shell is broken into — an electron is being removed from a shell closer to the nucleus.

Graphs like the one in Figure 1 can tell you which group of the periodic table an element belongs to. Just count how many electrons are removed before the first big jump to find the group number.

Example

In Figure 1, one electron is removed before the first big jump — sodium is in Group 1.

These graphs can be used to predict the electronic structure of an element. Working from right to left, count how many points there are before each big jump to find how many electrons are in each shell, starting with the first.

Example

Working from right to left in Figure 1, the graph has 2 points on the right-hand side, then a jump, then 8 points, a jump, and 1 final point. Sodium has 2 electrons in the first shell, 8 in the second and 1 in the third.

Practice Questions — Application

Q1 a) Write an equation for the second ionisation energy of boron.

b) Write an equation for the second ionisation energy of chlorine.

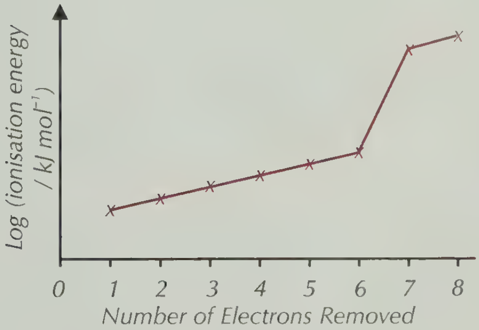
c) Write an equation for the third ionisation energy of chlorine.

Q2 Here is an ionisation energy equation for sulfur.

$$S^{4+}_{(g)} \rightarrow S^{5+}_{(g)} + e$$

Which ionisation energy does the equation show?

Q3 The graph below shows the successive ionisation energies of an element.



a) Which group is this element in?

b) State the number of electrons it has in each shell.

c) Name the element.

Q4 a) Sketch a graph showing the successive ionisation energies of magnesium.

b) Explain the shape of the graph.

Exam Tip

Make sure you use your periodic table to help you on questions like this. It can also help to write out electron configurations so that you can see what shell and orbital an electron is being removed from for each successive ionisation energy.

4. Giant Covalent Lattices

Learning Objectives:

- Explain the solid giant covalent lattices of carbon (diamond, graphite and graphene) and silicon as networks of atoms bonded by strong covalent bonds.
- Be able to use ideas about bonding to explain the strength and conductive properties of graphene, and its potential applications and benefits.
- Explain the physical properties of giant covalent lattices, including melting and boiling points, solubility and electrical conductivity in terms of structure and bonding.

Specification Reference 3.1.1

Atoms can form giant structures as well as tiny ones. Silicon and carbon both form giant structures — giant compared to other atomic structures, anyway...

Bonding in giant covalent lattices

Giant covalent lattices are huge networks of covalently bonded atoms. (They're sometimes called **macromolecular** structures.) Carbon and silicon atoms can form this type of structure because they can each form four strong, covalent bonds. Different forms of the same element in the same state are called **allotropes**. There are three carbon allotropes you need to know about — graphite, diamond and graphene.

Graphite

The carbon atoms in graphite are arranged in sheets of flat hexagons covalently bonded with three bonds each (see Figure 1). The fourth outer electron of each carbon atom is delocalised. The sheets of hexagons are bonded together by weak induced dipole-dipole forces (see pages 123-124).

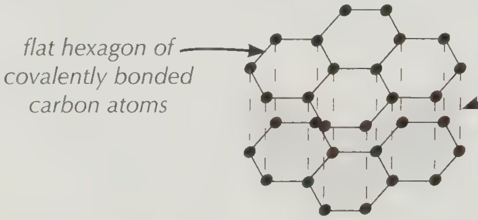

flat hexagon of covalently bonded carbon atoms
induced dipole-dipole forces

Figure 1: *The structure of graphite.*

Graphite's structure means it has certain properties:

- The weak forces between the layers in graphite are easily broken, so the sheets can slide over each other — graphite feels slippery and is used as a dry lubricant and in pencils.
- The 'delocalised' electrons in graphite are free to move along the sheets, so an electric current can flow.
- The layers are quite far apart compared to the length of the covalent bonds, so graphite has a low density and is used to make strong, lightweight sports equipment.
- Because of the strong covalent bonds in the hexagon sheets, graphite has a very high melting point (it sublimes at over 3900 K).
- Graphite is insoluble in any solvent. The covalent bonds in the sheets are too difficult to break.

Diamond

Diamond is also made up of carbon atoms. Each carbon atom is covalently bonded to four other carbon atoms (see Figure 2). The atoms arrange themselves in a tetrahedral shape — its crystal lattice structure.

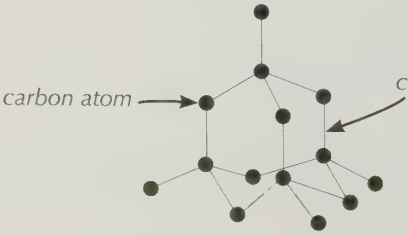


Figure 2: *The structure of diamond.*

Tip: 'Delocalised' means an electron isn't attached to a particular atom — it can move around between atoms.

Tip: 'Sublimes' means it changes straight from a solid to a gas, skipping out the liquid stage.

Tip: Tetrahedral is a molecular shape — see pages 116-119 for more on shapes of molecules.

Tip: You can 'cut' diamond to form gemstones (see Figure 3). Its structure makes it refract light a lot, which is why it sparkles.

Because it has lots of strong covalent bonds:

- Diamond has a very high melting point — it actually sublimes at over 3800 K.
- Diamond is extremely hard — it's used in diamond-tipped drills and saws.
- Vibrations travel easily through the stiff lattice, so it's a good thermal conductor.
- It can't conduct electricity — all the outer electrons are held in localised bonds.
- Like graphite, diamond won't dissolve in any solvent.

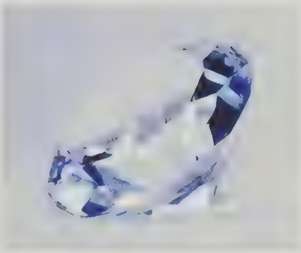


Figure 3: *A cut and polished diamond. Oooh, sparkly.*

Silicon

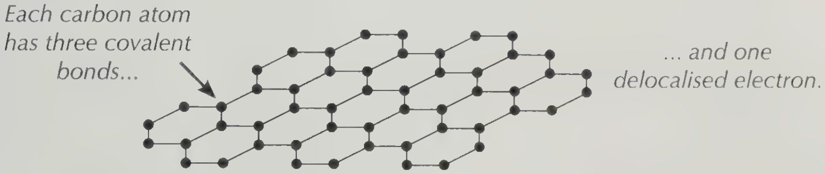
Silicon is in the same periodic group as carbon. Each silicon atom can also form four strong, covalent bonds. It makes a crystal lattice structure like diamond, and has similar properties.

Tip: Properties that can be directly perceived, like the fact that graphite is slippery or diamond is hard are called macroscopic properties. Finding explanations for macroscopic properties is important in science.

HOW SCIENCE WORKS

Graphene

Graphene is just one layer of graphite — it's a sheet of carbon atoms joined together in hexagons. The sheet is one atom thick, making it a two-dimensional compound.



Each carbon atom has three covalent bonds...
... and one delocalised electron.

Figure 4: *The structure of graphene.*

Graphene's structure gives it some pretty useful properties:

- Like in graphite, the delocalised electrons in graphene are free to move along the sheet. Without layers, they can move quickly above and below the sheet, making graphene the best known electrical conductor.
- The delocalised electrons also strengthen the covalent bonds between the carbon atoms. This makes graphene extremely strong.
- A single layer of graphene is transparent and incredibly light.

Due to its high strength, low mass, and good electrical conductivity, graphene has potential applications in high-speed electronics and aircraft technology. Its flexibility and transparency also make it a potentially useful material for touchscreens on smartphones and other electronic devices.

Tip: Like diamond and graphite, graphene has high melting and boiling points and it's insoluble due to its strong covalent bonds.

Tip: When new substances, like graphene, are discovered, scientists can start to consider how the properties of the material could be applied and what its benefits could be.

HOW SCIENCE WORKS

Practice Questions — Fact Recall

Q1 a) Describe the structure of diamond.
b) Explain why the structure of diamond means it can't conduct electricity.

Q2 Describe the structure of graphite.

Q3 a) Describe the structure of graphene.
b) Explain why the structure of graphene makes it a good electrical conductor.
c) Give an example of a potential application of graphene.

Learning Objectives:

- Describe metallic bonding as a strong electrostatic attraction between cations (positive ions) and delocalised electrons.
- Be able to describe giant metallic lattice structures.
- Explain the physical properties of giant metallic lattices, including melting and boiling points, solubility and electrical conductivity in terms of structure and bonding.

Specification Reference 3.1.1

5. Metallic Bonding

You'll be familiar with metallic bonding from GCSE, but there's more to know...

Metallic bonding

Metal elements exist as giant metallic lattice structures. The outermost electrons of a metal atom are delocalised — the electrons are free to move about the metal. This leaves a positive metal cation, e.g. Na^+, Mg^{2+}, Al^{3+}. The metal cations are electrostatically attracted to the delocalised electrons — they form a lattice of closely packed cations in a sea of delocalised electrons — this is metallic bonding (see Figure 1).

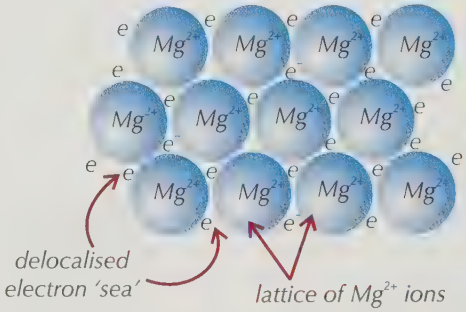


Figure 1: *Metallic bonding in magnesium.*

Metallic bonding explains the properties of metals — for example, their melting and boiling points, their ability to be shaped, their conductivity and their solubility.

Melting and boiling points

The number of delocalised electrons per atom affects the melting and boiling points. The more there are, the stronger the bonding will be and the higher the melting and boiling points. Mg^{2+} has two delocalised electrons per atom, so it's got higher melting and boiling points than Na^+, which only has one. The size of the metal ion and the lattice structure also affect the melting and boiling points. A smaller ionic radius will hold the delocalised electrons closer to the nuclei.

Ability to be shaped

As there are no bonds holding specific ions together, the metal ions can slide over each other when the structure is pulled, so metals are malleable (can be shaped) and ductile (can be drawn into a wire, see Figure 2).

Figure 2: *Copper pulled into a wire.*

Conductivity

The delocalised electrons can pass kinetic energy to each other, making metals good thermal conductors. Metals are good electrical conductors because the delocalised electrons can carry a charge.

Solubility

Metals are insoluble, except in liquid metals, because of the strength of the metallic bonds.

Practice Questions — Fact Recall

Q1 Describe the structure of magnesium.

Q2 What type of bonding can be found in magnesium?

Q3 Explain the following:

a) Copper can be drawn into wires.

b) Copper is a good thermal conductor.

6. Periodic Trends in Melting and Boiling Points

Melting and boiling points have periodicity, due to structure and bonding.

Learning Objectives:

- Explain the variation in melting and boiling points across Periods 2 and 3 in terms of structure and bonding.
- Understand the trend in structure from giant metallic to giant covalent to simple molecular lattice.

Specification Reference 3.1.1

Melting and boiling points

If you look at how the melting and boiling points change across the periods, the trend isn't immediately obvious. The melting and boiling points of the Period 2 and 3 elements generally increase from the first to the fourth elements in the period, but then decrease from the fourth to the eighth elements (see Figures 1 and 2).

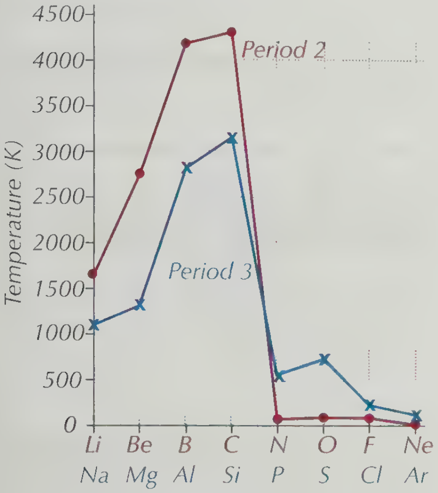


Figure 1: *The trend in boiling points across Periods 2 and 3.*

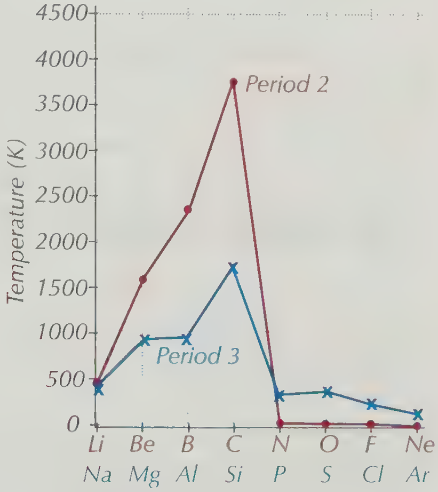


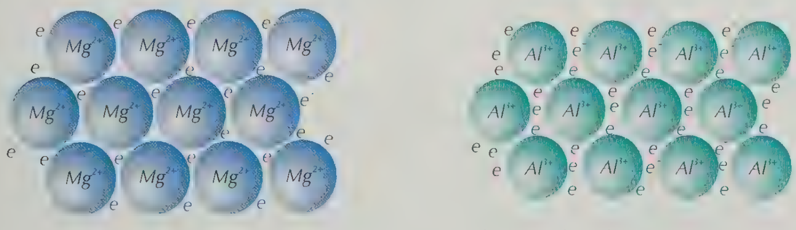
Figure 2: *The trend in melting points across Periods 2 and 3.*

Once you start looking at the bond strengths and structures of the elements in Periods 2 and 3, the reasons for the trends become clear. As you go across a period, the type of bonding between the atoms of an element and the type of structure changes. It changes from giant metallic to giant covalent and then to a simple molecular lattice.

Metals

For the metals (Li and Be, Na, Mg and Al), melting and boiling points increase across the period because the metal-metal bonds get stronger. The bonds get stronger because the metal ions have a greater charge, an increasing number of **delocalised electrons** and a decreasing ionic radius. This leads to a higher **charge density**, which attracts the ions together more strongly (see Figure 3).

Tip: The charge density is the amount of charge in relation to the size of an ion. Smaller ions have greater charge densities than larger ions with the same charge.



The magnesium ions have a larger radius and a charge of 2+ so there are two delocalised electrons for each ion...

...whereas the aluminium ions have a smaller radius and a charge of 3+ so there are three delocalised electrons for each ion.

Figure 3: *The structures of magnesium and aluminium.*

Giant covalent structures

The elements with giant covalent lattice structures (B, C and Si) have strong covalent bonds linking all their atoms together. A lot of energy is needed to break these bonds. So, for example, carbon and silicon have the highest melting and boiling points in their periods.

Simple molecular structures

Next come the simple molecular substances (N_2, O_2 and F_2 in Period 2 and P_4, S_8 and Cl_2 in Period 3). The covalent bonds between the atoms in a molecule are very strong but the melting and boiling points depend upon the strength of the induced dipole-dipole forces between their molecules. These forces are weak and easily overcome so these elements have low melting and boiling points.

Tip: See pages 123-127 for lots more about intermolecular forces.

More atoms in a molecule mean stronger induced dipole-dipole forces. For example, in Period 3 sulfur is the biggest molecule (S_8), so it's got higher melting and boiling points than phosphorus or chlorine — see Figure 4.

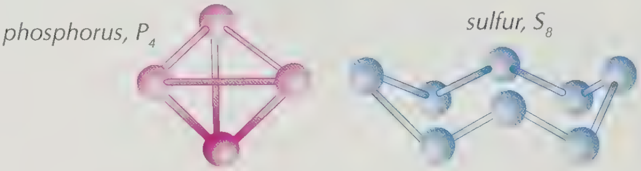


Figure 4: *The structures of phosphorus and sulfur.*

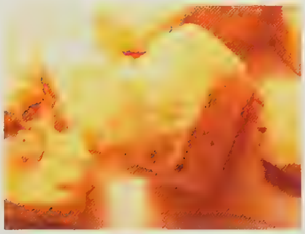


Figure 5: *Sulfur is a solid at room temperature.*

The noble gases (neon and argon) have the lowest melting and boiling points because they exist as individual atoms (they're monatomic) resulting in very weak induced dipole-dipole forces.

Practice Questions — Application

Q1 a) Explain why the boiling point of lithium is higher than the boiling point of nitrogen.

b) Explain why the boiling point of beryllium is higher than that of lithium.

Q2 a) Explain why magnesium has a higher melting point than sodium.

b) Explain why sulfur has a higher melting point than phosphorus.

Q3 The melting point of silicon is 1414 °C and the melting point of phosphorus is 44 °C.

a) Explain why the melting point of phosphorus is lower than the melting point of silicon.

b) Name a Period 3 element with a lower melting point than phosphorus.

Q4 Would you expect calcium to have a higher or lower boiling point than potassium? Explain your answer.

Practice Questions — Fact Recall

Q1 Describe the trend in melting and boiling points that occurs across Period 2 of the periodic table.

Q2 Name two Period 2 elements that have giant covalent lattice structures.

Q3 Name the Period 3 element that has the lowest melting point.

7. Group 2 — The Alkaline Earth Metals

The alkaline earth metals are in the s-block of the periodic table. You have to know some trends in their properties as you go down Group 2 and some of the reactions of Group 2 elements and their compounds.

Trend in reactivity down Group 2

When Group 2 elements react they lose electrons, forming positive ions (cations). The easier it is to lose electrons (i.e. the lower the first and second ionisation energies), the more reactive the element. So because ionisation energy decreases down the group, reactivity increases down the group.

Reactions of Group 2 elements

Group 2 elements all have two electrons in their outer shell (s^2). They can lose their two outer electrons to form 2+ ions. Their ions then have every atom's dream electronic structure — that of a **noble gas** (see Figure 1).

Element	Electronic structure	Ion	Electronic structure
Be	$1s^2\,2s^2$	Be^{2+}	$1s^2$
Mg	$1s^2\,2s^2\,2p^6\,3s^2$	Mg^{2+}	$1s^2\,2s^2\,2p^6$
Ca	$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2$	Ca^{2+}	$1s^2\,2s^2\,2p^6\,3s^2\,3p^6$

Figure 1: *Electronic structures of Group 2 atoms and ions.*

So, when Group 2 elements react, they are oxidised from a state of 0 to +2.

$$M \rightarrow M^{2+} + 2e^-$$

Oxidation state: $0 \rightarrow +2$

In this equation, M is used to represent any Group 2 metal.

Examples

$Mg \rightarrow Mg^{2+} + 2e^-$ $\quad$ $Ca \rightarrow Ca^{2+} + 2e^-$ $\quad$ $Be \rightarrow Be^{2+} + 2e^-$

Oxidation number: 0 $\quad$ +2 $\quad$ 0 $\quad$ +2 $\quad$ 0 $\quad$ +2

Reactions with water

The Group 2 metals react with water to give a metal hydroxide and hydrogen.

$$M_{(s)} + 2H_2O_{(l)} \rightarrow M(OH)_{2\,(aq)} + H_{2\,(g)}$$

Oxidation state: 0 $\rightarrow$ +2

The metal hydroxide that forms dissolves in water to produce hydroxide ions (OH^-). These make the solutions strongly alkaline, with a pH of about 12-13.

Example

Calcium reacts with water to form calcium hydroxide and hydrogen.

$$\mathbf{Ca_{(s)} + 2H_2O_{(l)} \rightarrow Ca^{2+}_{(aq)} + 2OH^-_{(aq)} + H_{2(g)}}$$

Oxidation state: 0 $\rightarrow$ +2

The hydrogen gas forms bubbles in the solution.

The elements react more readily down the group because the ionisation energies decrease (see Figure 4). This is due to the increasing size of the atomic radii and the increasing shielding effect (see page 136).

Learning Objectives:

- Know that the outer shell electron configuration of elements in Group 2 is s^2.
- Understand that the Group 2 elements lose their outer s^2 electrons in redox reactions to form 2+ ions.
- Know the relative reactivities of the Group 2 elements (from Mg to Ba) shown by their redox reactions with oxygen, water and dilute acids.
- Explain the trend in reactivity in terms of the first and second ionisation energies of Group 2 elements down the group.
- Know the effect of water on Group 2 oxides and the approximate pH of any resulting solutions, including the trend of increasing alkalinity.
- Know uses of some Group 2 compounds as bases, including equations. For example, the use of $Ca(OH)_2$ in agriculture to neutralise acid soils and the use of $Mg(OH)_2$ and $CaCO_3$ as 'antacids' for treating indigestion.

Specification Reference 3.1.2

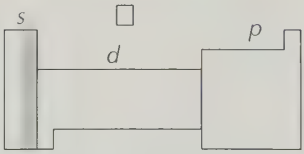


Figure 2: *The s-, p- and d-blocks of the periodic table (see page 134 for more). Group 2 is highlighted in grey.*

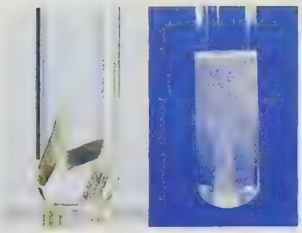


Figure 3: *Magnesium (left) and calcium (right) reacting with water. Calcium is more reactive so reacts quicker.*

Group 2 element	1st ionisation energy / kJ mol⁻¹	Rate of reactivity with water
Be	900	doesn't react
Mg	738	VERY slow
Ca	590	quite quick
Sr	550	quick
Ba	503	rapid

Figure 4: *Comparison of first ionisation energies and reactivity with water for Group 2 elements.*

Reactions with oxygen

When Group 2 metals burn in oxygen, you get solid white oxides. Here's the general equation for the reaction of a Group 2 metal (M) with oxygen.

$$2M_{(s)} + O_{2(g)} \rightarrow 2MO_{(s)}$$

Examples

Calcium burns in air to produce calcium oxide (CaO). The equation for this reaction is:

$$2Ca_{(s)} + O_{2\,(g)} \rightarrow 2CaO_{(s)}$$

Beryllium burns in air to produce beryllium oxide (BeO). Here's the equation:

$$2Be_{(s)} + O_{2\,(g)} \rightarrow 2BeO_{(s)}$$

As with the other reactions of Group 2 elements, during this reaction the oxidation state of the Group 2 element increases from 0 to +2.

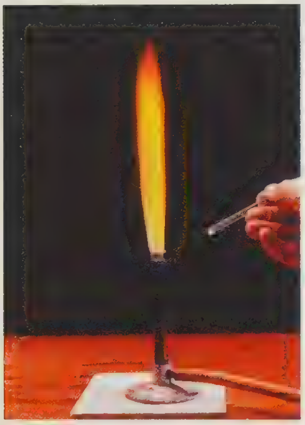


Figure 5: *Calcium burns in air, producing an orange flame.*

Tip: It's because their oxides form alkaline solutions that the Group 2 elements are also known as the alkaline earth metals.

Tip: An alkali is a base that's soluble in water. The oxides and hydroxides of Group 2 metals are bases. Most of them are also alkalis.

The oxides of the Group 2 metals react readily with water to form metal hydroxides, which dissolve. The hydroxide ions, OH^-, make these solutions strongly alkaline (e.g. pH 12 - 13).

Example

Calcium oxide reacts with water to form calcium hydroxide. The calcium hydroxide then dissolves in the water, releasing OH^- ions and Ca^{2+} ions. So,

$$CaO_{(s)} + H_2O_{(l)} \rightarrow Ca^{2+}_{(aq)} + 2OH^-_{(aq)}$$

The OH^- ions make the solution strongly alkaline.

Magnesium oxide is an exception — it only reacts slowly and the hydroxide isn't very soluble. The oxides form more strongly alkaline solutions as you go down the group, because the hydroxides get more soluble.

Reactions with dilute acids

When Group 2 metals react with dilute hydrochloric acid, you get a metal chloride and hydrogen. Here's the general equation for the reaction of a Group 2 metal (M) with dilute hydrochloric acid.

$$M_{(s)} + 2HCl_{(aq)} \rightarrow MCl_{2\,(aq)} + H_{2\,(g)}$$

Oxidation state: 0 → +2

Examples

Calcium reacts with dilute hydrochloric acid to produce calcium chloride ($CaCl_2$). The equation for this reaction is:

$$Ca_{(s)} + 2HCl_{(aq)} \rightarrow CaCl_{2(aq)} + H_{2(g)}$$

Strontium reacts with dilute hydrochloric acid to produce strontium chloride ($SrCl_2$). The equation for this reaction is:

$$Sr_{(s)} + 2HCl_{(aq)} \rightarrow SrCl_{2(aq)} + H_{2(g)}$$

Tip: The reactions of Group 2 metals with dilute acid get more vigorous as you go down the group — this is the same trend as with water.

Different acids will produce different salts. For example, if you use dilute sulfuric acid, you'll get a metal sulfate.

$$M_{(s)} + H_2SO_{4(aq)} \rightarrow MSO_{4(aq)} + H_{2(g)}$$

Example

Magnesium reacts with dilute sulfuric acid to produce magnesium sulfate ($MgSO_4$). The equation for this reaction is:

$$Mg_{(s)} + H_2SO_{4(aq)} \rightarrow MgSO_{4(aq)} + H_{2(g)}$$

Uses of Group 2 compounds

Group 2 elements are known as the **alkaline earth metals**, and many of their common compounds are used for neutralising acids. Here are a couple of common examples:

- Calcium hydroxide (slaked lime, $Ca(OH)_2$) is used in agriculture to neutralise acid soils. It has to be used in moderation though, otherwise the soils will become too alkaline to support crop growth.
- Magnesium hydroxide ($Mg(OH)_2$) and calcium carbonate ($CaCO_3$) are used in some indigestion tablets as **antacids** — these neutralise excess stomach acid.

In both cases, the ionic equation for the neutralisation is:

$$H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)}$$

Figure 6: *Tractors are used to spread slaked lime to neutralise acid soil.*

Practice Questions — Application

Q1 When calcium reacts with water, calcium hydroxide is produced.
  a) Write an equation for this reaction.
  b) How does the oxidation state of calcium change during this reaction?
  c) State what you would see when this reaction takes place.
  d) How would the rate of the reaction be different if strontium was used instead of calcium?

Q2 Strontium burns in air to form strontium oxide.
  a) Write an equation for this reaction.
  b) Describe the appearance of strontium oxide.
  c) Write an equation to show what would happen if water was added to strontium oxide.
  d) Give an approximate pH of the solution formed when water and strontium oxide are mixed.

Tip: When writing equations for reactions don't forget to make sure they're balanced.

Exam Tip

You're often asked to apply your knowledge of trends to say how or why one reaction would be different from another. Start by finding the elements involved on the periodic table and seeing whether they are in the same group or the same period. The trends across groups and periods are different.

Q3 Calcium reacts with hydrochloric acid to form calcium chloride.
  a) Write an equation for this reaction.
  b) How does the oxidation state of calcium change during this reaction?
  c) State what you would see when this reaction takes place.
  d) Predict how the rate of reaction would be different if barium was used instead of calcium.

Practice Questions — Fact Recall

Q1 Explain why reactivity increases down Group 2.

Q2 a) What charge do Group 2 ions usually have?
  b) Explain why Group 2 ions normally have this charge.

Q3 What change in oxidation state do Group 2 metals usually undergo when they react?

Q4 What pH would you expect a Group 2 metal hydroxide solution to have?

Q5 Which, out of barium oxide and strontium oxide, would you expect to be more alkaline?

Q6 Describe the trend in the reactivity of the Group 2 elements with dilute acids as you go down the group.

Q7 Give two uses of Group 2 hydroxides.

8. Group 7 — The Halogens

The halogens are highly-reactive non-metals found in Group 7 of the periodic table. You need to know about their properties, trends and reactions.

Properties of halogens

The table below gives some of the main properties of the first four halogens, at room temperature. They exist as diatomic molecules (molecules made up of two atoms).

halogen	formula	colour	physical state	electronic structure
fluorine	F_2	pale yellow	gas	$1s^2\ 2s^2\ 2p^5$
chlorine	Cl_2	green	gas	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$
bromine	Br_2	red-brown	liquid	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^5$
iodine	I_2	grey	solid	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^2\ 5p^5$

Figure 1: *Some properties of the first four halogens.*

Trend in boiling points

The boiling and melting points of the halogens increase down the group. This is due to the increasing strength of the **induced dipole-dipole** (London) **forces** as the number of electrons increases when the size and relative mass of the atoms increases. This trend is shown in the changes of physical state from fluorine to iodine (see Figure 2). A substance is said to be **volatile** if it has a low boiling point. So you could also say that volatility decreases down the group.

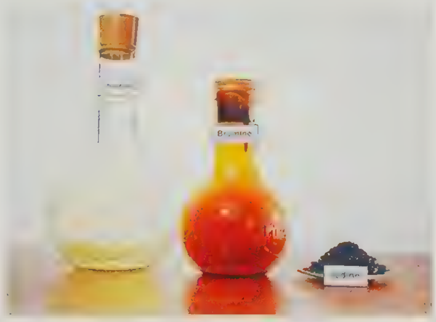


Figure 2: *At room temperature and pressure, chlorine (left) is a gas, bromine (centre) is a liquid and iodine (right) is a solid.*

Trend in reactivity

Halogen atoms react by gaining an electron in their outer shell. This means they're reduced. When halogens are reduced, **halide** ions are formed. The general equation for the reduction of a halogen (X) to a halide ion (X^-) is shown below:

$$\begin{array}{lccc} & X + e^- & \rightarrow & X^- \\ \textit{oxidation number:} & 0 & & -1 \end{array}$$

As the halogens are reduced, they oxidise another substance (it's a redox reaction — see pages 99-101) — so they're **oxidising agents**.

As you go down the group, the atomic radius increases so the outer electrons are further from the nucleus. The outer electrons are also shielded more from the attraction of the positive nucleus, because there are more inner electrons. This makes it harder for larger atoms to attract the electron needed to form an ion (despite the increased charge on the nucleus), so larger atoms are less reactive. Another way of saying that the halogens get less reactive down the group is to say that they become less oxidising.

Learning Objectives:

- Know that halogens exist as diatomic molecules.
- Explain the trend in the boiling points of Cl_2, Br_2 and I_2 in terms of induced dipole-dipole interactions.
- Know the outer shell configuration of Group 7 elements and that they'll gain one electron in many redox reactions to form 1– ions.
- Understand the trend in reactivity of the halogens Cl_2, Br_2 and I_2, illustrated by reactions with other halide ions.
- Explain the trend in reactivity in terms of attraction, atomic radius and electron shielding.
- Know the precipitation reactions of the aqueous anions Cl^-, Br^- and I^- with aqueous silver ions, followed by aqueous ammonia, and their use as a test for different halide ions.
- Be able to use apparatus to carry out qualitative tests for ions, and make and record your observations (PAG 4).

Specification Reference 3.1.3

Tip: Halogen should be used when describing the atom (X) or molecule (X_2), but halide is used to describe the negative ion (X^-).

Displacement reactions

The halogens' relative oxidising strengths can be seen in their **displacement reactions** with halide ions. More reactive halogens will oxidise and displace the halide ions of less reactive halogens. Reactivity decreases down the group so a halogen will displace a halide from solution if the halide is below it in the periodic table. You need to know which halogens displace what and the **ionic equations** for these displacement reactions.

Tip: The displacement reactions of the halogens can be used to identify them in solution. See the next page for more.

Halogen	Displacement reactions	Ionic equations
Cl	chlorine (Cl_2) will displace bromide (Br^-) and iodide (I^-)	$Cl_{2(aq)} + 2Br^-_{(aq)} \rightarrow 2Cl^-_{(aq)} + Br_{2(aq)}$ $Cl_{2(aq)} + 2I^-_{(aq)} \rightarrow 2Cl^-_{(aq)} + I_{2(aq)}$
Br	bromine (Br_2) will displace iodide (I)	$Br_{2(aq)} + 2I^-_{(aq)} \rightarrow 2Br^-_{(aq)} + I_{2(aq)}$
I	no reaction with F^-, Cl^-, Br^-	

Figure 3: *Some displacement reactions of the halogens.*

Tip: These are ionic equation — they only show the reacting particles.

When these displacement reactions happen, there are colour changes — you can see what happens by following them.

Examples

Bromine water and potassium iodide

If you mix bromine water, $Br_{2\,(aq)}$, with potassium iodide solution, the bromine displaces the iodide ions (it oxidises them), giving iodine (I_2) and potassium bromide solution, $KBr_{(aq)}$. The equation for this reaction is:

$$Br_{2(aq)} + 2I^-_{(aq)} \rightarrow 2Br^-_{(aq)} + I_{2(aq)}$$

Oxidation number of Br: 0 → −1

Oxidation number of I: −1 → 0

Iodine water ($I_{2\,(aq)}$) is brown and bromine water ($Br_{2\,(aq)}$) is orange. So when bromine displaces the iodide ions in potassium iodide, the solution changes colour from orange to brown.

Chlorine water and potassium bromide

If you mix chlorine water, $Cl_{2\,(aq)}$, with potassium bromide, $KBr_{(aq)}$, the solution changes from colourless to orange. The chlorine displaces the bromide ions, forming bromine water ($Br_{2(aq)}$), which is orange.

$$Cl_{2(aq)} + 2Br^-_{(aq)} \rightarrow 2Cl^-_{(aq)} + Br_{2(aq)}$$

Oxidation number of Cl: 0 → −1

Oxidation number of Br: −1 → 0

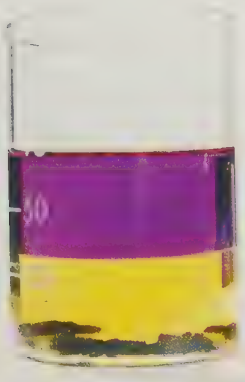


Figure 4: *Iodine mixed with hexane (an organic solvent). The top layer shows the violet colour of the solution formed when iodine dissolves in hexane. The bottom layer is an aqueous solution of I_2.*

Brown and orange can sometimes look a bit similar. You can make the changes easier to see by shaking the reaction mixture with an organic solvent like hexane. The halogen that's present will dissolve readily in the organic solvent, which settles out as a distinct layer (called the solvent layer) above the aqueous solution. The different halogens are very different colours when they are dissolved in organic solvent so you can easily see which halogen has been produced.

- A violet/pink colour shows the presence of iodine (see Figure 4).
- An orange/red colour shows bromine.
- A very pale yellow/green shows chlorine.

Tip: Make sure you learn all of these colour changes. You'll need them for the exam.

The table on the next page summarises the colour changes you'll see when different displacement reactions take place.

	Potassium chloride solution ($KCl_{(aq)}$)	Potassium bromide solution ($KBr_{(aq)}$)	Potassium iodide solution ($KI_{(aq)}$)
Chlorine water ($Cl_{2(aq)}$) – colourless		orange/red solution (Br_2) formed with organic solvent	violet/pink solution (I_2) formed with organic solvent
Bromine water ($Br_{2(aq)}$) – orange	No reaction		violet/pink solution (I_2) formed with organic solvent
Iodine solution ($I_{2(aq)}$) – brown	No reaction	No reaction	

Figure 5: *The results of some reactions between halogens and halide compounds.*

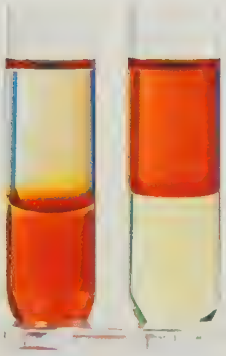


Figure 6: *The initial (left) and final (right) appearance of a test tube when an organic solvent is added to bromine water. Notice the red/orange colour of the solvent layer which settles at the top of the test tube.*

Identifying halogens in solution

The halogen displacement reactions can be used to help identify which halogen or halide is present in a solution. All you have to do is mix your unknown solution with some known halogen solutions and watch to see what colour changes take place.

Examples

Chlorine water is added to a solution of an unknown potassium halide. When hexane is added, an organic solvent layer forms which is violet in colour. Identify the halide ions present in the unknown solution.

Because the organic solvent layer turns violet, you know that I_2 must have been formed. So, I^- ions must have been present in the unknown solution. When the chlorine water is added the following reaction occurs:

$$Cl_{2(aq)} + 2I^-_{(aq)} \rightarrow 2Cl^-_{(aq)} + I_{2(aq)}$$

An unknown halogen solution is added to solutions of KBr and KCl. A colour change occurs with KBr but not with KCl. Identify the halogen present in the unknown solution.

Because there is a colour change when the halogen solution is added to KBr, you know that a displacement reaction has occurred and Br_2 has been formed. So the halogen can't be I_2 or Br_2 because neither of these can displace Br^- ions. Because no colour change happens when the unknown halogen solution is added to KCl you know the halogen can't be F_2 (because this would displace the Cl^- ions). So the unknown halogen must be Cl_2.

Exam Tip
You could be asked to identify any halogen or halide solution in your exam so make sure you learn which reactions happen and what the colour changes are.

Tip: When identifying halogen or halide solutions, looking at which reactions don't happen is as important as looking at the reactions that do happen.

Testing for halides

PRACTICAL ACTIVITY GROUP 4

The halogens are pretty distinctive to look at. Unfortunately, halide ions aren't so easily identifiable. Luckily, you can test for halides using the silver nitrate test — it's dead easy.

- If you're testing solid substances for halide ions, you'll first need to dissolve each of them separately in distilled water to make solutions.
- Once you've got solutions of the substances that you're testing, use a pipette to add about 3 cm^3 of each solution to separate test tubes.
- Label each test tube so that you don't get confused about which solution is which.

Tip: You won't ever be asked to identify fluorine in school or college — it's too hazardous. But it's still worth knowing how to identify it.

Tip: Remember, you should carry out a risk assessment before doing any practicals, and take any necessary precautions.

Tip: You can't use hydrochloric acid instead of nitric acid because the silver nitrate would just react with the chloride ions from the HCl — and that would mess up your results completely.

Tip: Be careful when handling $AgNO_3$ — it can stain skin and clothing. Also take great care with concentrated NH_3 as it's corrosive.

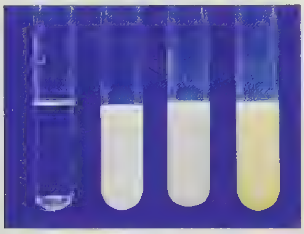


Figure 8: *Results of silver nitrate tests for solutions containing (L-R) fluoride, chloride, bromide and iodide ions.*

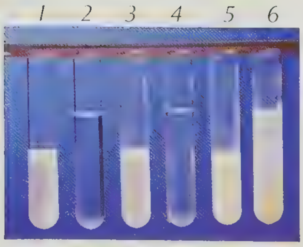


Figure 9: *The chloride, bromide and iodide test tubes from Figure 8 (1, 3 and 5), and the same tubes with concentrated $NH_{3(aq)}$ added (2, 4 and 6).*

- Prepare a table to record your results. You'll need to include each sample that you're testing, and leave space to record whether a precipitate is formed with silver nitrate.
- Using a pipette, add a few drops of dilute nitric acid (HNO_3) to each test tube. This gets rid of any unwanted ions that might otherwise mess up the test results.
- Again using a pipette, add a few drops of aqueous silver nitrate ($AgNO_{3(aq)}$) to each test tube. If there are chloride, iodide or bromide ions present a precipitate of the silver halide will be formed.

  $$Ag^+_{(aq)} + X^-_{(aq)} \rightarrow AgX_{(s)} \quad \text{...where X is Cl, Br or I}$$

  The colour of the precipitate identifies the halide (see Figures 7 and 8). You should record your observations in your results table.

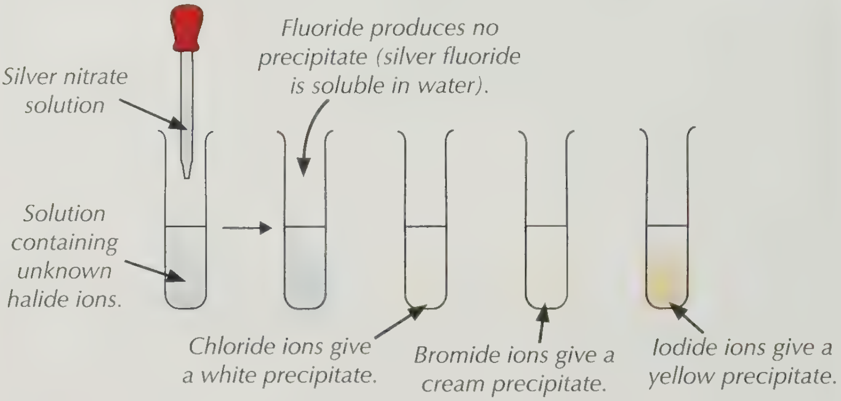

Silver nitrate solution
Fluoride produces no precipitate (silver fluoride is soluble in water).
Solution containing unknown halide ions.
Chloride ions give a white precipitate.
Bromide ions give a cream precipitate.
Iodide ions give a yellow precipitate.

Figure 7: *The silver nitrate test for identifying an unknown halide ion in solution.*

It isn't always easy to tell the difference between silver halide precipitates — some of them look very similar (see Figure 8). So there's a further test that you can carry out using dilute or concentrated ammonia that makes it much easier to tell the halides apart. Before you start, you'll have to add a column to your results table to record your observations for what happens to each of the halide precipitates when dilute or concentrated ammonia solution is added.

- Using a pipette, add dilute ammonia (NH_3) to each of the silver halide precipitate suspensions. You should add about the same amount of ammonia as the amount of silver halide precipitate suspension you have.
- Stir the mixtures using a glass rod and record whether any precipitates dissolve in the ammonia.
- If any precipitates haven't dissolved, add concentrated ammonia to the solution. Add roughly the same volume of concentrated ammonia as you did dilute ammonia.
- Again, stir the mixtures using a glass rod, and record whether the precipitates dissolve.
- You should now be able to identify which halides were in your samples. Each silver halide has a different solubility in ammonia — the larger the ion is, the more difficult it is to dissolve (see Figures 9 and 10).

Halide	Result
Chloride Cl^-	precipitate dissolves in dilute $NH_{3(aq)}$
Bromide Br^-	precipitate doesn't dissolve in dilute $NH_{3(aq)}$ but will dissolve in conc. $NH_{3(aq)}$
Iodide I^-	precipitate is insoluble in dilute and conc. $NH_{3(aq)}$

Figure 10: *Solubility of silver halide precipitates in ammonia.*

Practice Questions — Application

Q1 Explain why the boiling point of bromine is lower than that of iodine.

Q2 Chlorine water is mixed with potassium iodide.

a) Write out the ionic equation for the reaction, along with the change in oxidation numbers of both halogens.

b) Hexane is added to the solution. What do you expect to see?

Q3 Fluorine is the most reactive of the halogens. Explain why the other halogens are less reactive than fluorine.

Q4 When bromine is added to an unknown solution of halide ions and an organic solvent is added, the solvent layer turns violet.

a) Identify the halide ions present in the solution.

b) Write an equation for the displacement reaction that occurs.

Q5 An experiment is carried out to identify the halide ions in three different solutions. The results are shown in the table below.

Sample	*Colour of precipitate following addition of silver nitrate*	*Effect of adding concentrated NH_3 solution to the precipitate*
A	*yellow*	*no change*
B	*no precipitate*	*no change*
C	*cream*	*precipitate dissolves*

Identify the halide ion in each sample.

Practice Questions — Fact Recall

Q1 What is a diatomic molecule?

Q2 Describe and explain the trend in the boiling points of the halogens.

Q3 Explain why the halogens get less reactive as you go down the group.

Q4 Which halide ions are displaced by reaction with chlorine water?

Q5 What colour is the organic layer when an organic solvent is added to:

a) chlorine water b) bromine water c) iodine water

Q6 Briefly describe a test for distinguishing between different halide solutions.

9. Disproportionation and Water Treatment

Learning Objectives:

- Be able to explain the term disproportionation as oxidation and reduction of the same element.
- Know that the reaction of chlorine with cold, dilute aqueous sodium hydroxide is a disproportionation reaction and is used to form bleach.
- Be able to describe analogous reactions to the reaction of chlorine with cold, dilute aqueous sodium hydroxide using other halogens.
- Know that the reaction of chlorine with water is a disproportionation reaction and is used in water purification, and be able to describe analogous reactions using other halogens.
- Be able to contrast the benefits of chlorine use in water treatment with its associated risks.

Specification Reference 3.1.3

Disproportionation doesn't have a snappy name and it's got far more letters than you expect, but it is quite handy — and you have to know all about it for your exam.

Disproportionation reactions

Disproportionation is when a single element is simultaneously oxidised and reduced. The halogens undergo disproportionation when they react with cold dilute alkali solutions (e.g. NaOH or KOH). The general equation for the reaction of a halogen (X) with sodium hydroxide (NaOH) is shown below:

$$\begin{array}{llllllll} \textit{Full equation:} & X_2 & + & 2NaOH & \rightarrow & NaXO & + NaX & + H_2O \\ \textit{Ionic equation:} & X_2 & + & 2OH^- & \rightarrow & XO^- & + X^- & + H_2O \\ \textit{Oxidation number of X:} & 0 & & & & +1 & -1 & \end{array}$$

All of the halogens, except fluorine, can exist in oxidation states other than the 0 and –1 oxidation states.

–1	0	+1
Cl^-	Cl_2	ClO^-
chloride	chlorine	chlorate(I)

Figure 1: *Some of the oxidation states of chlorine.*

Example

Bromine reacts with NaOH to give sodium bromate(I), sodium bromide and water:

$$Br_{2(aq)} + 2NaOH_{(aq)} \rightarrow NaBrO_{(aq)} + NaBr_{(aq)} + H_2O_{(l)}$$

As Br_2, bromine has an oxidation state of 0. In NaBrO the oxidation state of bromine is +1, so when bromine forms NaBrO it is oxidised. In NaBr the oxidation state of bromine is –1, so when bromine forms NaBr it is reduced. So in the reaction above, the bromine is simultaneously oxidised and reduced and it is a disproportionation reaction.

Making bleach

If you mix chlorine gas with cold, dilute aqueous sodium hydroxide, you get sodium chlorate(I) solution, $NaClO_{(aq)}$, which just happens to be common household bleach. In this reaction some of the chlorine is oxidised and some of it is reduced so it's a disproportionation reaction.

$$2NaOH_{(aq)} + Cl_{2(g)} \rightarrow NaClO_{(aq)} + NaCl_{(aq)} + H_2O_{(l)}$$

Chlorine is bonded to chlorine so its oxidation state is 0.

ClO^- is the chlorate(I) ion. Chlorine's oxidation state is +1 in this ion.

Here, chlorine's oxidation state is –1.

Tip: Don't get disproportionation and displacement reactions mixed up. See page 152 for more on displacement reactions.

Tip: Take a look at pages 95-97 for more on oxidation states and how to work them out.

The sodium chlorate(I) solution (bleach) has loads of uses — it's used in water treatment, to bleach paper and textiles... and it's good for cleaning toilets, too. Handy...

Chlorine and water

When you mix chlorine with water, it undergoes disproportionation. You end up with a mixture of hydrochloric acid and chloric(I) acid (also called hypochlorous acid).

$$\underset{\nearrow}{Cl_{2(g)}} + H_2O_{(l)} \rightleftharpoons \underset{\nearrow}{HCl_{(aq)}} + \underset{\nwarrow}{HClO_{(aq)}}$$

Chlorine's oxidation state is 0.

In hydrochloric acid, chlorine's oxidation state is –1.

In chloric(I) acid, chlorine's oxidation state is +1.

Aqueous chloric(I) acid ionises to make chlorate(I) ions (also called hypochlorite ions):

$$HClO_{(aq)} + H_2O_{(l)} \rightleftharpoons ClO^-_{(aq)} + H_3O^+_{(aq)}$$

Tip: Bromine and iodine can both react with water in similar equilibrium reactions to produce HX and HXO (where X is a halogen).

Figure 2: *Chlorine is used to treat tap water in the UK.*

Water treatment

Chlorate(I) ions kill bacteria. So, adding chlorine (or a compound containing chlorate(I) ions) to water can make it safe to drink or swim in. In the UK our drinking water is treated to make it safe.

Chlorine is an important part of water treatment. It kills disease-causing microorganisms (and some chlorine persists in the water and prevents reinfection further down the supply). It also prevents the growth of algae, eliminating bad tastes and smells, and removes discolouration caused by organic compounds.

HOW SCIENCE WORKS

However, there are risks from using chlorine to treat water. Chlorine gas is toxic. It's very harmful if it's breathed in — it irritates the respiratory system. Liquid chlorine on the skin or eyes causes severe chemical burns. Accidents involving chlorine could be really serious, or fatal. Water contains a variety of organic compounds, e.g. from the decomposition of plants. Chlorine reacts with these compounds to form chlorinated hydrocarbons, e.g. chloromethane (CH_3Cl), and many of these chlorinated hydrocarbons are carcinogenic (cancer-causing). However, this increased cancer risk is small compared to the risks from untreated water — a cholera epidemic, say, could kill thousands of people. There are ethical considerations too. We don't get a choice about having our water chlorinated — some people object to this as forced 'mass medication'.

Tip: See page 4 for more about weighing up the benefits and risks of scientific techniques (like using chlorine to treat drinking water).

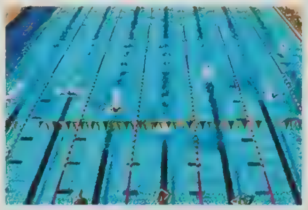


Figure 3: *The distinctive 'swimming pool smell' is due to the chlorine in the water.*

Alternatives to chlorine

There are other methods of purifying drinking water. And just like chlorine, they have their advantages and disadvantages.

- Ozone (O_3) is a strong oxidising agent, which makes it great at killing microorganisms. However, it's expensive to produce and its short half-life in water means that treatment isn't permanent.
- Ultraviolet light kills microorganisms by damaging their DNA, but it is ineffective in cloudy water and, like O_3, it won't stop the water being contaminated further down the line.

Practice Questions — Application

Q1 When iodine is mixed with dilute potassium hydroxide solution (KOH) a disproportionation reaction occurs.

a) Write an equation to show the reaction of iodine with KOH.

b) Using oxidation states, explain why this reaction is a disproportionation reaction.

Q2 The equation below shows the decomposition of hydrogen peroxide (H_2O_2) to water and oxygen:

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

Is this a disproportionation reaction? Explain your answer.

Tip: The oxidation state of oxygen in H_2O_2 is –1, the oxidation state of oxygen in H_2O is –2 and the oxidation state of oxygen in O_2 is 0.

Q3 The equation below shows the reaction of chlorine gas with water:

$$Cl_{2(g)} + H_2O_{(l)} \rightleftharpoons HCl_{(aq)} + HClO_{(aq)}$$

a) Write an equation to show how chlorate(I) ions can be produced from one of the products of this reaction.

b) Explain why chlorate(I) ions are added to water.

Practice Questions — Fact Recall

Q1 What is disproportionation?

Q2 a) Name the three products of the reaction between sodium hydroxide and chlorine.

b) Give the balanced equation for this reaction.

Q3 Describe the reactions that occur when chlorine is mixed with water.

Q4 a) Explain why chlorine is used to treat water.

b) Describe the disadvantages of using chlorine to treat water.

Q5 Ozone is sometimes used in water treatment.

a) Why is ozone good for water treatment?

b) What are the drawbacks of using ozone?

c) Name another alternative to chlorine in water treatment.

10. Tests for Ions

PRACTICAL ACTIVITY GROUP 4

If you're given something and asked to find out what's in it, there are loads of different tests that you can do — here are just a few...

False positives

When you're carrying out tests to identify an unknown substance you need to be wary of creating false positive results. A false positive is a result that suggests that a particular ion is present when it actually isn't. This can happen if there are ions present that will interfere with the test you are carrying out. To prevent false positive you can sometimes add a substance to your sample to remove problematic ions. You also need to be careful about what substances you add during the test — it's important not to add any ions that will lead to false positives. To help prevent false positives, you should do the three tests below in the following order:

Test for carbonates ⟶ Test for sulfates ⟶ Test for halides

Test for carbonates

If you have an unknown solution and you want to test it for carbonates (CO_3^{2-}), add a dilute strong acid (e.g. dilute nitric acid or dilute hydrochloric acid). If carbonates are present then carbon dioxide will be released. The ionic equation for the reaction of a carbonate and an acid is:

$$\underset{\text{carbonate}}{CO_3^{2-}{}_{(s)}} + \underset{\text{acid}}{2H^+_{(aq)}} \rightarrow \underset{\text{carbon dioxide}}{CO_{2(g)}} + \underset{\text{water}}{H_2O_{(l)}}$$

Example

Calcium carbonate reacts with hydrochloric acid to produce carbon dioxide, water and calcium chloride. The equation for this reaction is:

$$CaCO_{3(s)} + 2HCl_{(aq)} \rightarrow CO_{2(g)} + H_2O_{(l)} + CaCl_{2(aq)}$$

You can test to see if the gas produced is carbon dioxide using limewater. Figure 1 shows the apparatus needed for this test.

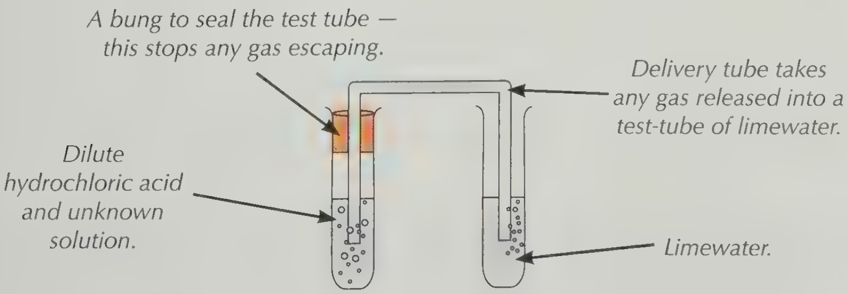

A bung to seal the test tube — this stops any gas escaping.
Delivery tube takes any gas released into a test-tube of limewater.
Dilute hydrochloric acid and unknown solution.
Limewater.

Figure 1: *Apparatus for carrying out a test for carbonate ions.*

Any gas created by the reaction is delivered into limewater — if it's CO_2, then it'll react and turn the limewater cloudy (see Figure 2).

Learning Objectives:

- Understand how to use qualitative analysis to identify the ions in an unknown compound on a test-tube scale.
- Be able to use apparatus to carry out qualitative tests for ions, and make and record your observations (PAG 4).
- Be able to identify CO_3^{2-} ions by reaction with $H^+_{(aq)}$, forming $CO_{2(g)}$.
- Be able to identify SO_4^{2-} ions by precipitation with $Ba^{2+}_{(aq)}$.
- Be able to identify Cl^-, Br^- and I^- ions.
- Be able to identify NH_4^+ ions by reaction with warm $NaOH_{(aq)}$, forming NH_3.

Specification Reference 2.1.4, 3.1.3, 3.1.4

Tip: Think about any safety precautions you might need to consider before doing these tests.

Tip: Carrying out experiments and investigations correctly is an important part of scientific enquiry.

HOW SCIENCE WORKS

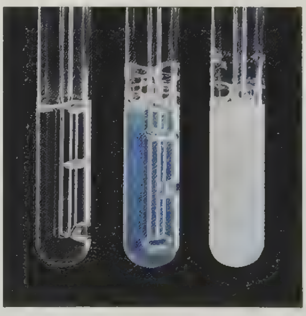


Figure 2: *Limewater turns cloudy when carbon dioxide is added to it.*

Tip: You can carry out the test for carbonates on solids as well as solutions — just add a small amount of your solid to a test-tube containing the acid.

You can carry out this test on a test-tube scale, so you'll only need to use small volumes of the substances. Transfer the liquids into the test tubes using teat pipettes. Make sure you place the bung connected to the transfer tube on to the test tube quickly after adding the acid to the solution, so that you don't lose too much of any gas produced.

Test for sulfates

Tip: You could also test for sulfates by using barium chloride solution, $BaCl_{2(aq)}$, instead of barium nitrate solution.

If you carried out the test for carbonates and didn't get a positive result, i.e. no CO_2 was produced, then you can move on to test for sulfates ions. Most sulfates are soluble in water, but barium sulfate is insoluble. So, to test for a sulfate ion (SO_4^{2-}), add a few drops of barium nitrate solution, $Ba(NO_3)_{2\,(aq)}$, to a solution of the unknown substance. If you get a white precipitate it'll be barium sulfate, which tells you your mystery substance is a sulfate (see Figure 3). However, you need to be careful you don't end up with a false positive due to carbonate or sulfite ions.

Tip: You don't need to remember this equation, but you need to understand why you have to avoid this reaction when testing for sulfates.

Example

Sodium sulfite reacts with $Ba(NO_3)_2$ solution to give barium sulfite and sodium nitrate:

$$Na_2SO_{3\,(s)} + Ba(NO_3)_{2\,(aq)} \rightarrow BaSO_{3\,(s)} + 2NaNO_{3(aq)}$$

Barium sulfite is a white precipitate, which will confuse the results of a test for sulfates.

Figure 3: Barium sulfate is a white precipitate.

In the test for carbonates, you add a dilute strong acid to your substance. The acid will react with any carbonates or sulfites present, which makes sure that they won't interfere with the test for sulfates and cause a false positive. So if you haven't done the test for carbonates on your sample already, you'll need to add dilute acid before you add any barium nitrate, in order to remove any carbonate or sulfite ions that may be in the solution.

Now that you've got rid of any carbonates or sulfites, if a white precipitate is formed from the reaction with barium nitrate solution, it can only mean that sulfate ions are present. The ionic equation for this reaction is:

$$\begin{array}{ccccc} SO_4{}^{2-}{}_{(aq)} & + & Ba^{2+}{}_{(aq)} & \rightarrow & BaSO_{4\,(s)} \\ \text{sulfate anion} & + & \text{barium cation} & \rightarrow & \text{barium sulfate} \end{array}$$

Tip: You test for halides after you test for sulfates because silver sulfate (Ag_2SO_4) is insoluble. If you tested for halides before testing to see if the anions were sulfate, then any precipitate you see might be a false positive — it could be silver sulfate rather than a silver halide.

Example

Sodium sulfate reacts with $Ba(NO_3)_2$ solution to give barium sulfate and sodium nitrate:

$$Na_2SO_{4\,(s)} + Ba(NO_3)_{2\,(aq)} \rightarrow BaSO_{4\,(s)} + 2NaNO_{3\,(aq)}$$

If no precipitate is formed, you don't have any sulfate ions present and you can then move on to the last test.

Test for halides

Tip: Silver fluoride is soluble, so it won't give any precipitate.

To test for halide ions just add nitric acid, then silver nitrate solution. If chloride, bromide or iodide is present, a precipitate will form. The colour of the precipitate depends on the halide present — silver chloride (AgCl) is a white precipitate, silver bromide (AgBr) is a cream precipitate and silver iodide (AgI) is a yellow precipitate.

It might not be easy to distinguish between the different colours of precipitate, so you can test the solubility of them in ammonia to help you tell them apart — look back at pages 153-154 for more details about this test.

Test for ammonium ions

Ammonia gas (NH_3) is alkaline, so you can check for it using a damp piece of red litmus paper. If there's ammonia present, the paper will turn blue (see Figure 4). You'll also be able to smell ammonia — it has a distinctive, pungent smell.

You can use this to test whether a substance contains ammonium ions (NH_4^+). Add a few drops of aqueous sodium hydroxide to your mystery substance in a test tube and warm the mixture. Hold a piece of damp litmus paper near the top of the test-tube. If the paper turns blue it means ammonia is being given off and there are ammonium ions in your substance. The ionic equation for this reaction is:

$$NH_4^+{}_{(aq)} + OH^-{}_{(aq)} \rightarrow NH_{3(g)} + H_2O_{(l)}$$

ammonium ion + hydroxide ion → ammonia + water

Example

Ammonium chloride reacts with sodium hydroxide to give ammonia, water and sodium chloride.

$$NH_4Cl_{(aq)} + NaOH_{(aq)} \rightarrow NH_{3(g)} + H_2O_{(l)} + NaCl_{(aq)}$$

Practice Questions — Application

Q1 An unknown solution is run through a series of tests to determine what ions are present.
Firstly, dilute hydrochloric acid is added. The gas produced is delivered into limewater. The limewater does not change.
Next, barium chloride is added to the solution.
A white precipitate is formed.
What ions are present in the unknown solution?

Q2 A student adds barium nitrate solution to an unknown solution to try and determine what ions are present. A white precipitate is formed and he concludes that there are sulfate ions in the unknown solution.

a) Explain why he might be wrong.

b) Suggest how he should carry out the test to correctly determine the presence of sulfate ions.

Practice Questions — Fact Recall

Q1 What is the correct order in which you should carry out the tests for:
sulfates, carbonates, halides?

Q2 Name a dilute acid used in the test for:
a) carbonates b) sulfates c) halides

Q3 What colour will red litmus paper go in the presence of ammonia?

Tip: If you used barium chloride solution in the test for sulfates, or have added hydrochloric acid at any point, then you'll need to carry out the test for halides using a fresh sample of the unknown substance. This is because the chloride ions you've introduced to the sample could give a false positive.

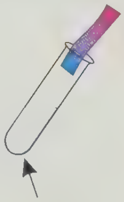


Figure 4: Ammonia will come out of solution when heated and turn damp litmus paper blue.

Tip: The litmus paper needs to be damp so the ammonia gas can dissolve and make the colour change.

Exam Tip
If you're asked how to test for a particular ion in the exam, or you're asked to draw conclusions from a set of results, you need to think about what ions could be present that could give false positives. Have they been dealt with or could they interfere with the test? Also, remember to always consider the effect that adding substances during a test could have. Have ions been added that will affect the results?

Section Summary

Make sure you know...

- How the periodic table was developed, and its acceptance by the scientific community.
- That in the modern periodic table the elements are arranged in order of increasing atomic number.
- That the modern periodic table is organised into periods (rows), groups (columns) and blocks (e.g. the s-block, p-block and d-block).
- That the elements within a period all have the same number of electron shells (ignoring sub-shells).
- That periods show repeating trends in physical and chemical properties and that this is known as periodicity.
- That the elements within a group all have the same number of electrons in their outer shell and as a result have similar physical and chemical properties.
- How the periodic table can be used to work out the electron configuration of an element.
- What first ionisation energy and successive ionisation energies are.
- Why first ionisation energy generally increases across a period and decreases down a group.
- Why first ionisation energy decreases between Groups 2 and 3, and between Groups 5 and 6.
- That trends in ionisation energy support the Bohr model of the atom.
- How to use successive ionisation energies of an element to work out how many electrons are in each of its shells and what group it's in.
- That carbon (as diamond, graphite and graphene) and silicon have giant covalent lattice structures.
- How the properties of the allotropes of carbon can be explained by their structure and bonding.
- That metals have a giant metallic structure that's held together by electrostatic attraction between cations and delocalised electrons and how this determines its properties.
- The variation in melting and boiling points as you move across Periods 2 and 3.
- How to explain the variation in melting and boiling points across Periods 2 and 3 in terms of structure and bonding.
- That the Group 2 elements generally form M^{2+} ions when they react because this gives them a stable electron configuration (that of a noble gas).
- Why the Group 2 elements get more reactive as you move down the group.
- That the Group 2 elements undergo redox reactions with water to form metal hydroxides and hydrogen gas, that they burn in air to form metal oxides, and that they react with dilute acids to form metal salts and hydrogen gas.
- That the Group 2 oxides are solid white powders which react with water to form alkaline solutions with a pH of 12–13.
- That some Group 2 compounds are bases that can be used to neutralise soil and as antacids.
- Why the boiling and melting points of the halogens increase as you move down Group 7.
- Why the halogens get less reactive as you move down Group 7.
- How halogen and halide ion solutions can be identified using displacement reactions.
- How to use silver nitrate and ammonia solution to test for halide ions.
- That a disproportionation reaction is a reaction where a single element is simultaneously oxidised and reduced.
- How bleach is formed, using chlorine and sodium hydroxide, and its uses.
- The equations for the reactions of chlorine with water.
- The benefits and risks of using chlorine in water treatment.
- How to test for carbonates, sulfates and halides, and in which order the tests should be carried out.
- How to test for ammonium ions.

Exam-style Questions

1 The table below shows the first six ionisation energies of a Period 3 element.

ionisation number	1st	2nd	3rd	4th	5th	6th
ionisation energy (kJ mol^{-1})	577.5	1816.7	2744.8	11577	14842	18379

What is the element?

A Sodium

B Aluminium

C Phosphorus

D Chlorine

(1 mark)

2 When chlorine undergoes disproportionation with potassium hydroxide, the reaction produces potassium chloride, potassium chlorate and water.

Which of the options below gives the correct oxidation states of chlorine in each molecule?

	Cl_2	KCl	KClO
A	0	–1	+1
B	–1	–1	0
C	0	+1	–1
D	–1	0	+1

(1 mark)

3 Below are four statements about ionisation energies.

1. The increase in ionisation energy between Groups 5 and 6 is due to electron repulsion.
2. The 3rd ionisation energy of an element is always higher than the 2nd ionisation energy.
3. The drop in ionisation energy between Groups 2 and 3 is due to the electrons that are removed being in different orbitals.
4. The number of neutrons in the nucleus of an atom affects its ionisation energies.

Which of these statements are true?

A Only 1, 2 and 3.

B Only 2 and 3.

C Only 1 and 3.

D Only 2 and 4.

(1 mark)

4 The periodic table is a table of elements arranged into periods and groups.

(a) (i) Identify the fifteenth element in Period 4 of the periodic table.

State which block of the periodic table this element is in.

(1 mark)

(ii) Use your knowledge of the periodic table to write the electronic configuration for this element.

(1 mark)

(b) Strontium and barium are both in Group 2 of the periodic table. Both react with oxygen forming solid white oxides.

(i) Write equations, including state symbols, for the reactions of strontium and barium with oxygen.

(2 marks)

(ii) Use your knowledge of the periodic table to explain why strontium and barium react with oxygen in similar ways.

(2 marks)

(iii) Explain how the rate of the reaction of strontium with oxygen is likely to be different from the reaction of barium with oxygen.

(2 marks)

5 The elements in Group 2 of the periodic table are commonly known as the alkaline earth metals.

The alkaline earth metals react with water to form metal hydroxides.

(a) (i) Write a balanced equation for the reaction of calcium with water.

(1 mark)

(ii) Give the electron configuration of the calcium species before and after it reacts with water.

(1 mark)

(iii) Describe what you would see when this reaction takes place.

(2 marks)

(iv) State the approximate pH of the resulting calcium hydroxide solution.

(1 mark)

(b) (i) Give one use of calcium hydroxide.

(1 mark)

(ii) Write an ionic equation for the reaction that takes place when calcium hydroxide is used in this way.

(1 mark)

6 A student was demonstrating that an unknown potassium halide solution was potassium bromide.

(a) He mixed some of the solution with chlorine water ($Cl_{2(aq)}$) and added hexane. Then he observed the results.

(i) Write an ionic equation for the displacement reaction that would occur if the solution was potassium bromide.

(1 mark)

(ii) State how the colour of the organic solvent layer could be used to distinguish between a solution of potassium bromide and potassium iodide.

(2 marks)

(b) The student's results confirmed that the solution was potassium bromide. The student further confirmed his results using the silver nitrate test.

(i) Describe how the student could perform a silver nitrate test to confirm that bromide ions were present in the unknown solution.

(2 marks)

(ii) Write an ionic equation, including state symbols, for the reaction that occurs when a silver nitrate test is used to detect bromide ions.

(1 mark)

(iii) Explain how the student could double-check his results.

(2 marks)

7 Carbon is the first element of Group 4.

(a) Different forms of the same element in the same state are called allotropes. Carbon has three common allotropes.

(i) Name three common allotropes of carbon.

(1 mark)

(ii) Silicon is also a Group 4 element.

Which allotrope of carbon has the same structure as silicon?

(1 mark)

(iii) Describe the lattice structure of silicon.

(2 marks)

(b) Carbon and nitrogen are both in Period 2.

(i) Explain why the first ionisation energy of carbon is lower than that of nitrogen.

(3 marks)

(ii)* Carbon has the highest melting point of all the elements in Period 2.

Explain why the melting points of Period 2 elements change as you move across the period.

Your answer should include details of the structure and bonding of the Period 2 elements.

(6 marks)

*The quality of your response will be assessed in this question.

Learning Objectives:

- Explain and use the terms standard conditions and standard states.
- Define and use the terms enthalpy change of reaction, enthalpy change of formation, enthalpy change of combustion and enthalpy change of neutralisation.
- Explain that some chemical reactions are accompanied by enthalpy changes that can be exothermic (ΔH negative) or endothermic (ΔH positive).
- Construct an enthalpy profile diagram for a reaction to show the difference in the enthalpy of the reactants compared with that of the products.
- Explain qualitatively, using enthalpy profile diagrams, the term activation energy.

Specification Reference 3.2.1

1. Enthalpy Changes

When chemical reactions happen, some bonds are broken and some bonds are made. More often than not, this'll cause a change in energy. The souped-up chemistry term for this is enthalpy change.

Enthalpy notation

Enthalpy change, ΔH (delta H), is the heat energy transferred in a reaction at constant pressure. The units of ΔH are kJ mol^{-1}. You write ΔH° to show that the measurements were made under **standard conditions** and that the elements were in their **standard states** (i.e. their physical states under standard conditions). Standard conditions are 100 kPa (about 1 atm) pressure and a temperature of 298 K (25 °C). Sometimes the notation will also include a subscript to signify the type of reaction. See below for more on this notation.

Conditions for enthalpy changes

You can't directly measure the actual enthalpy of a system. In practice, that doesn't matter, because it's only ever enthalpy change that matters. You can find enthalpy changes either by experiment or in data books. Enthalpy changes you find in data books are usually standard enthalpy changes — enthalpy changes under standard conditions (298 K and 100 kPa). This is important because changes in enthalpy are affected by temperature and pressure — using standard conditions means that everyone can know exactly what the enthalpy change is describing.

The different types of ΔH

Standard enthalpy change of reaction

Standard enthalpy change of reaction, $\Delta_r H^\circ$, is the enthalpy change when a reaction occurs in the molar quantities shown in the chemical equation, under standard conditions with all reactants and products in their standard states.

Standard enthalpy change of formation

Standard enthalpy change of formation, $\Delta_f H^\circ$, is the enthalpy change when 1 mole of a compound is formed from its elements in their standard states under standard conditions, e.g. $2C_{(s)} + 3H_{2(g)} + ½O_{2(g)} \rightarrow C_2H_5OH_{(l)}$.

Standard enthalpy change of combustion

Standard enthalpy change of combustion, $\Delta_c H^\circ$, is the enthalpy change when 1 mole of a substance is completely burned in oxygen under standard conditions with all reactants and products in their standard states.

Standard enthalpy change of neutralisation

Standard enthalpy change of neutralisation, $\Delta_{neut} H^\circ$, is the enthalpy change when solutions of an acid and an alkali react together to form 1 mole of water, under standard conditions.

Exothermic reactions

Exothermic reactions give out energy to their surroundings. The products of the reaction end up with less energy than the reactants. This means that the enthalpy change for the reaction, ΔH, will be negative.

Examples

Oxidation is usually exothermic. Here are two examples:

The combustion of a fuel like methane:

$$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)} \qquad \Delta_c H^\circ = -890 \text{ kJ mol}^{-1}$$

ΔH is negative so the reaction is **exothermic**.

The oxidation of carbohydrates, like glucose, in respiration is exothermic.

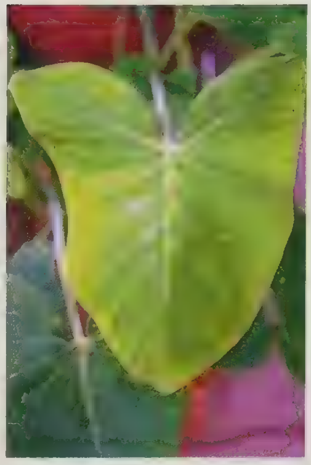


Figure 1: Photosynthesis in plants is endothermic — the products have more energy than the reactants.

Endothermic reactions

Endothermic reactions take in energy from their surroundings. This means that the products of the reaction have more energy than the reactants, so the enthalpy change for the reaction, ΔH, is positive.

Examples

The thermal decomposition of calcium carbonate is endothermic.

$$CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)} \qquad \Delta_r H^\circ = +179 \text{ kJ mol}^{-1}$$

ΔH is positive so the reaction is **endothermic**.

The main reactions of photosynthesis are also endothermic — sunlight supplies the energy.

Enthalpy profile diagrams

Enthalpy profile diagrams show you how the enthalpy (energy) changes during a reaction (see Figure 2). A substance is most stable when it has lost all of its internal energy. So, lower positions on an enthalpy profile diagram will be more stable than higher positions.

The **activation energy**, E_a, is the minimum amount of energy needed to begin breaking reactant bonds and start a chemical reaction. On an enthalpy diagram, E_a is the difference between the highest point and the energy of the reactants (see Figure 2).

Exam Tip

There's quite a bit of maths in this section but you need to learn the definitions too — you can be asked to write them down in an exam, and it's often the thing that people forget or get wrong.

Tip: On enthalpy profile diagrams ΔH arrows should point up for endothermic changes and down for exothermic changes.

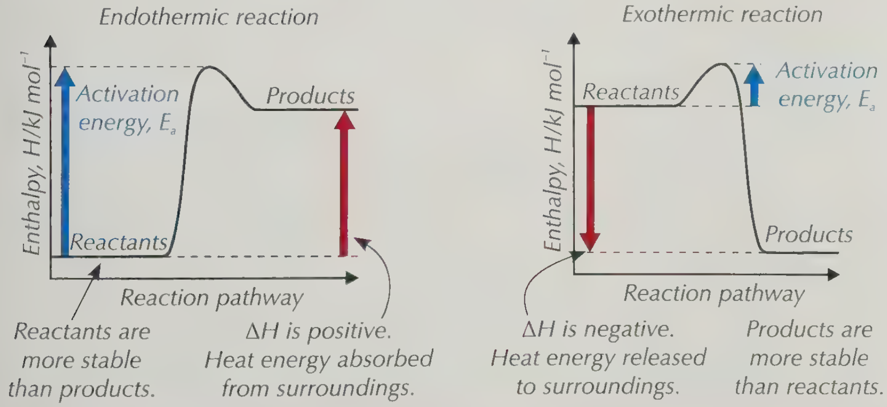

Endothermic reaction
Enthalpy, H/kJ mol⁻¹
Activation energy, Eₐ
Products
Reactants
Reaction pathway
Reactants are more stable than products.
ΔH is positive. Heat energy absorbed from surroundings.
Exothermic reaction
Enthalpy, H/kJ mol⁻¹
Reactants
Activation energy, Eₐ
Products
Reaction pathway
ΔH is negative. Heat energy released to surroundings.
Products are more stable than reactants.

Figure 2: *Enthalpy profile diagrams.*

Practice Questions — Fact Recall

Q1 Give the notation for an enthalpy change under standard conditions.

Q2 Define the 'standard enthalpy change of reaction'.

Q3 Describe the difference between exothermic and endothermic reactions.

Q4 a) Sketch an enthalpy profile diagram for an endothermic reaction.

b) Draw an arrow on the diagram to show E_a and explain the term.

2. Bond Enthalpies

Reactions involve breaking and making bonds. The enthalpy change for a reaction depends on which bonds are broken and which are made.

Learning Objectives:

- Explain exothermic and endothermic reactions in terms of enthalpy changes associated with the breaking and making of chemical bonds.
- Explain the term average bond enthalpy.
- Be able to calculate an enthalpy change of reaction and related qualities from average bond enthalpies.

Specification Reference 3.2.1

What are bond enthalpies?

In ionic bonding, positive and negative ions are attracted to each other. In covalent molecules, the positive nuclei are attracted to the negative charge of the shared electrons in a covalent bond. You need energy to break this attraction. The amount of energy you need per mole is called the bond dissociation enthalpy. (Of course it's got a fancy name — this is chemistry.) Bond dissociation enthalpies always involve bond breaking in gaseous compounds. This makes comparisons between different bond dissociation enthalpies fair.

Breaking and making bonds

When reactions happen, reactant bonds are broken and product bonds are formed. You need energy to break bonds, so bond breaking is endothermic (ΔH is positive). Stronger bonds take more energy to break. Energy is released when bonds are formed, so this is exothermic (ΔH is negative). Stronger bonds release more energy when they form. The enthalpy change for a reaction is the overall effect of these two changes. If you need more energy to break bonds than is released when bonds are made, ΔH is positive. If it's less, ΔH is negative.

Example

Nitrogen reacts with hydrogen to form ammonia in this reaction:

$$N_2 + 3H_2 \rightarrow 2NH_3$$

The energy needed to break all the bonds in N_2 and H_2 = 2253 kJ mol^{-1}.

The energy released when forming the bonds in NH_3 = 2346 kJ mol^{-1}.

The amount of energy released is bigger than the amount needed, so the reaction is exothermic and ΔH is negative. (See page 169 for full calculation.)

Tip: You can look up the average bond enthalpies for different bonds in a data book, or calculate them from given data. In an exam you'll be given any bond enthalpies you need.

Average bond enthalpies

We tend to use **average bond enthalpies** in calculations because the energy required to break an individual bond can change depending on where it is.

Example

Water (H_2O) has two O–H bonds (see Figure 1). You'd think it'd take the same amount of energy to break them both, but it doesn't.

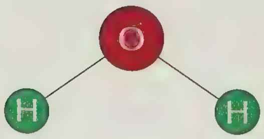


Figure 1: The bonds in a water molecule.

The first bond, $H\text{–}OH_{(g)}$: $E(H\text{–}OH) = +492$ kJ mol^{-1}

The second bond, $H\text{–}O_{(g)}$: $E(H\text{–}O) = +428$ kJ mol^{-1}

(OH^- is a bit easier to break apart because of the extra electron repulsion.)

So, the average bond enthalpy for O–H bonds in water is:

$$\frac{492 + 428}{2} = +460 \text{ kJ mol}^{-1}.$$

The data book says the bond enthalpy for O–H is +463 kJ mol^{-1}. It's a bit different than the one calculated above because it's the average for a much bigger range of molecules, not just water. For example, it includes the O–H bonds in alcohols and carboxylic acids too.

So when you look up an average bond enthalpy, what you get is the energy needed to break one mole of bonds in the gas phase, averaged over many different compounds.

Tip: This explanation of average bond energy is really important so make sure you learn it.

Calculating enthalpy changes

In any chemical reaction, energy is absorbed to break bonds and given out during bond formation. The difference between the energy absorbed and released is the enthalpy change of reaction:

Enthalpy change of reaction = Total energy absorbed – Total energy released

- To calculate the enthalpy change for a reaction, first calculate the total energy needed to break the bonds in the reactants. You'll usually be given the average bond enthalpies for each type of bond, so just multiply each value by the number of each bond present. This total will be the total energy absorbed in the reaction.
- To find the total energy released by the reaction, calculate the total energy needed to form all the new bonds in the products. Use the average bond enthalpies to do this.
- The overall enthalpy change for the reaction can then be found by subtracting the total energy released from the total energy absorbed.

Bond	Bond Enthalpy (Average value except where stated)
N≡N	+945 kJ mol^{-1}
H–H	+436 kJ mol^{-1}
N–H	+391 kJ mol^{-1}
O=O	+498 kJ mol^{-1}
O–H (water)	+460 kJ mol^{-1}

Figure 2: *Table of bond enthalpies.*

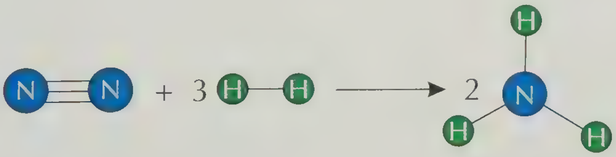
Examples — **Maths Skills**

Calculate the enthalpy change for the following reaction:

$$N_2 + 3H_2 \rightarrow 2NH_3$$

Use the bond enthalpy values shown in Figure 2.

You might find it helpful to draw a sketch of the molecules in the reaction:



Bonds broken: 1 × N≡N bond broken = 1 × 945 = 945 kJ mol^{-1}
3 × H–H bonds broken = 3 × 436 = 1308 kJ mol^{-1}

Total Energy Absorbed = 945 + 1308 = 2253 kJ mol^{-1}

Bonds formed: 6 × N–H bonds formed = 6 × 391 = 2346 kJ mol^{-1}
Total Energy Released = 2346 kJ mol^{-1}

Now you just subtract 'total energy released' from 'total energy absorbed':

Enthalpy change of reaction = 2253 – 2346 = –93 kJ mol^{-1}.

The negative sign tells you that the reaction is exothermic. More energy is released when the N–H bonds are made than is needed to break the N≡N and H–H bonds.

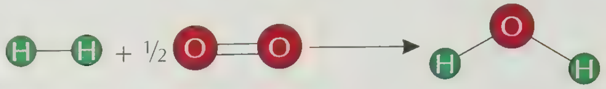
Tip: Draw sketches to show the bonds present in the reactants and products to make sure you include them all in your calculations.

Tip: If you can't remember which value to subtract from which, just take the smaller number from the bigger one then add the sign at the end — positive if 'bonds broken' was the bigger number (endothermic), negative if 'bonds formed' was bigger (exothermic).

Calculate the overall enthalpy change for the following reaction:

$$H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(g)}$$

The molecules present are shown below:



Bonds broken: 1 × H–H bond broken = 1 × 436 = 436 kJ mol^{-1}
½ × O=O bond broken = ½ × 498 = 249 kJ mol^{-1}

Total Energy Absorbed = 436 + 249 = 685 kJ mol^{-1}

Bonds formed: 2 × O–H bonds formed = 2 × 460 = 920 kJ mol^{-1}
Total Energy Released = 920 kJ mol^{-1}

Enthalpy change of reaction = 685 – 920 = –235 kJ mol^{-1}.

Tip: The $\frac{1}{2}O_2$ doesn't mean you're breaking ½ an O=O double bond — it means you're breaking ½ a mole of O=O double bonds.

Exam tip
Always double check you've multiplied the enthalpy values by the right number of bonds. It's really easy to make a mistake and end up losing marks.

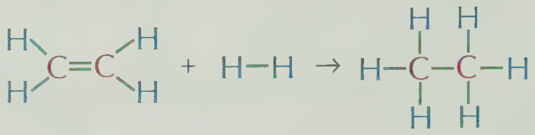
Tip: You can ignore any bonds that don't actually change during the reaction. Just work out which bonds actually break and which new bonds form. You'll still get the same value if you break and form all of the bonds, but it'll save you time if you don't have to.

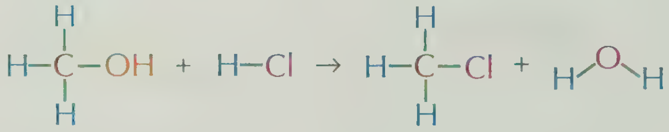
Bond	Bond Enthalpy (Average value except where stated)
C–H	+413 kJ mol^{-1}
C=C	+612 kJ mol^{-1}
C–C	+347 kJ mol^{-1}
C–O	+358 kJ mol^{-1}
C–Cl	+346 kJ mol^{-1}
C=O (in CO_2)	+805 kJ mol^{-1}
C–N	+286 kJ mol^{-1}
H–Cl	+432 kJ mol^{-1}
Cl–Cl	+243 kJ mol^{-1}

Figure 3: Table of bond enthalpies.

Practice Questions — Application

Q1 Use the average bond enthalpies shown in Figures 2 and 3 to calculate the enthalpy changes for the following reactions:

a)


b)


c) $C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$

d) $C_2H_5Cl + NH_3 \rightarrow C_2H_5NH_2 + HCl$

Q2 Calculate the enthalpy change for the complete combustion of ethene (C_2H_4) using the bond enthalpies given in Figures 2 and 3. (The products of complete combustion are CO_2 and H_2O.)

Q3 Calculate the standard enthalpy change of reaction for 1 mole of hydrogen ($H_{2(g)}$) reacting with 1 mole of chlorine ($Cl_{2(g)}$) to form hydrogen chloride ($HCl_{(g)}$) using the bond enthalpies given in Figures 2 and 3.

Q4 The enthalpy change for the following reaction is –181 kJ mol^{-1}:

$$2NO_{(g)} \rightarrow N_{2(g)} + O_{2(g)}$$

Use this value for $\Delta_r H^\circ$, along with the data in Figure 2, to estimate a value for the average bond enthalpy for the bond between nitrogen and oxygen in NO.

Practice Questions — Fact Recall

Q1 Is bond breaking exothermic or endothermic?

Q2 In an exothermic reaction, which is larger — the energy required to make bonds or the energy required to break bonds?

Q3 What is average bond enthalpy?

Q4 Give the formula for calculating the enthalpy change of a reaction.

3. Measuring Enthalpy Changes

A lot of the data we have on enthalpy changes has come from someone, somewhere, measuring the enthalpy change of a reaction in a lab.

Measuring enthalpy changes in the lab

PRACTICAL ACTIVITY GROUP 3

To measure the enthalpy change for a reaction, there are only two things you need to find out — the number of moles of the stuff that's reacting, and the change in temperature. How you go about doing the experiment depends on what type of reaction it is. Some reactions will quite happily take place in solution, such as neutralisation or displacement, and you can just stick a thermometer in to find out the temperature change. Use an insulated container like a polystyrene beaker, so that you don't lose or gain much heat through the sides (see Figure 1).

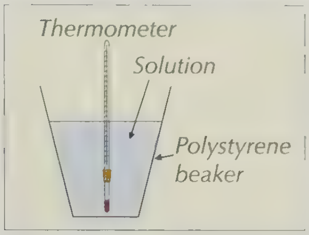


Figure 1: *Simple equipment used to measure the enthalpy change of reaction.*

Combustion reactions are trickier because the reactant is burned in air. A copper calorimeter containing a known mass of water is often used (see Figure 2). You burn a known mass of the reactant and record the temperature change of the water.

Ideally all the heat given out by the fuel as it burns would be absorbed by the water — allowing you to work out the enthalpy change of combustion (see page 166). In practice though, you always lose some heat (as you heat the apparatus and the surroundings).

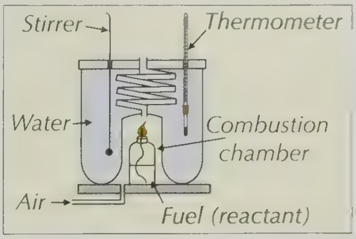


Figure 2: *A copper calorimeter used to measure the enthalpy change of combustion.*

A 'bomb' calorimeter, like the one shown in Figure 3, is a much more accurate piece of equipment, but works on the same principle.

Using the equation $q = mc\Delta T$

The equation for enthalpy change is:

$$q = mc\Delta T$$

q *= heat lost or gained (in J). This is the same as the enthalpy change if the pressure is constant.*

ΔT *= the change in temperature (in K or °C) of the solution / water.*

m *= mass (in g) of solution in the insulated container (or mass of water in the calorimeter).*

c *= specific heat capacity of the solution / water (4.18 J $g^{-1}K^{-1}$).*

Learning Objective:

- Describe the techniques and procedures used to determine enthalpy changes directly.
- Be able to calculate enthalpy changes directly from appropriate experimental results including use of the relationship: $q = mc\Delta T$.
- Be able to determine enthalpy changes from temperature measurements (PAG 3).

Specification Reference 3.2.1

HOW SCIENCE WORKS

Tip: Learning how to carry out experiments is an important part of science. We wouldn't get very far without experiments.

Tip: Before carrying out experiments in the lab, remember to carry out a risk assessment.

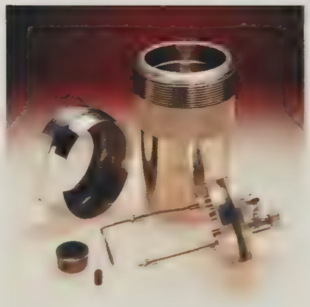


Figure 3: *A bomb calorimeter.*

Tip: The specific heat capacity of a substance is the amount of heat energy it takes to raise the temperature of 1 g of that substance by 1 K.

Tip: ΔH° is the standard enthalpy change of a reaction carried out at 100 kPa with all reactants and products in their standard states (see page 166). If the experiment was carried out under different conditions, this method wouldn't give you the value for ΔH°.

Figure 4: A combustion reaction — glucose burning.

Tip: M_r is the relative molecular mass — and it's exactly the same as the molar mass (M), except M_r doesn't have any units.

Exam Tip
You might be asked to suggest why a measured enthalpy change value is different to one in a data book. It's usually to do with heat losses to the surroundings, but it can also be due to things like incomplete combustion.

Calculating the standard enthalpy change of combustion

To calculate the standard enthalpy change of combustion, $\Delta_c H^\circ$, using data from a laboratory experiment, follow these steps:

Step 1: Calculate the amount of heat lost or gained during the combustion using $q = mc\Delta T$ and your measured or given values of m and ΔT. You'll then need to change the units of q from joules to kilojoules.

Step 2: Calculate the number of moles of fuel that caused this enthalpy change, from the mass that reacted. Use the equation:

$$n = \frac{\text{mass}}{M}$$

n is the number of moles of fuel burned.
M is the fuel's molar mass (see page 49).

Step 3: Calculate the standard enthalpy change of combustion, $\Delta_c H^\circ$ (in kJ mol^{-1}), using the actual heat change for the reaction, q (in kJ), and the number of moles of fuel that burned, n. Use the equation:

$$\Delta_c H^\circ = \frac{q}{n}$$

Example **Maths Skills**

Calculating the standard enthalpy change of combustion:

In a laboratory experiment, 1.16 g of an organic liquid fuel was completely burned in oxygen. The heat formed during this combustion raised the temperature of 100 g of water from 295.3 K to 357.8 K. Calculate the standard enthalpy of combustion, $\Delta_c H^\circ$, of the fuel. Its M_r is 58.0.

Step 1: Calculate the amount of heat given out by the fuel using $q = mc\Delta T$. Remember that m is the mass of water, not the mass of fuel.

$q = mc\Delta T$

$q = 100 \times 4.18 \times (357.8 - 295.3) = 26\,125 \text{ J}$

Change the amount of heat from J to kJ: $q = 26.125$ kJ.

Step 2: Find out how many moles of fuel produced this heat:

$$n = \frac{\text{mass}}{M} = \frac{1.16 \text{ g}}{58.0 \text{ g mol}^{-1}} = 0.0200 \text{ moles of fuel.}$$

Step 3: The standard enthalpy of combustion involves 1 mole of fuel.

$$\text{So } \Delta_c H^\circ = \frac{q}{n} = \frac{-26.125 \text{ kJ}}{0.0200 \text{ mol}} \approx -1310 \text{ kJ mol}^{-1} \text{ (3 s.f.).}$$

(Note: q is negative because combustion is an exothermic reaction.)

The actual $\Delta_c H^\circ$ of this compound is -1615 kJ mol^{-1} — loads of heat has been lost and not measured. E.g. it's likely a fair bit would escape through the copper calorimeter and also the fuel might not combust completely.

Calculating the standard enthalpy change of reaction

The standard enthalpy change of a reaction, $\Delta_r H^\circ$, is calculated in a slightly different way. Instead of calculating the enthalpy change per mole of substance reacted, you need to find the enthalpy change for the number of moles shown in the balanced chemical equation. Step 1 is exactly the same as step 1 for calculating the standard enthalpy change of combustion. It's steps 2 and 3 that are a bit different...

Step 2: Calculate the number of moles of one of the reactants that caused this enthalpy change, from the mass of it that reacted. Use the equation $n = \text{mass} \div M$ again.

Step 3: Calculate the standard enthalpy change of reaction, $\Delta_r H^{\circ}$ (in kJ mol^{-1}) using the actual heat change for the reaction, q (in kJ), and the number of moles that reacted, n, using the equation:

$$\Delta_r H^{\circ} = \frac{q}{n} \text{ (× number of moles reacting in balanced chemical equation)}$$

Tip: When finding the standard enthalpy change of a reaction, always write out a balanced equation for the reaction so you can see the correct molar quantities.

Example — Maths Skills

Calculating the standard enthalpy change of reaction:

30.0 g of ammonium chloride ($NH_4Cl_{(s)}$) is dissolved in water in a polystyrene beaker. The temperature of the contents of the beaker decreases from 298.0 K to 296.0 K. The total mass of the solution is 980 g. Calculate the standard molar enthalpy change for the reaction.

The balanced reaction is: $NH_4Cl_{(s)} \rightarrow NH_4^+{}_{(aq)} + Cl^-{}_{(aq)}$

The molar mass, M, of $NH_4Cl = 14.0 + (4 \times 1.0) + 35.5 = 53.5 \text{ g mol}^{-1}$.

Step 1: $q = mc\Delta T = 980 \times 4.18 \times (298.0 - 296.0) = 8192.8 \text{ J} = 8.1928 \text{ kJ}$

Step 2: $n = \dfrac{30.0 \text{ g}}{53.5 \text{ g mol}^{-1}} = 0.5607$ moles of NH_4Cl.

Step 3: The balanced reaction involves one mole of NH_4Cl so:

$$\Delta_r H^{\circ} = \frac{q}{n} = \frac{8.1928 \text{ kJ}}{0.5607 \text{ mol}} \approx +14.6 \text{ kJ mol}^{-1} \text{ (3 s.f.)}.$$

Tip: It doesn't matter whether you're measuring the temperature of pure water or a solution of something, always make the assumption that $c = 4.18 \text{ J g}^{-1} \text{ K}^{-1}$.

Practice Questions — Application

Q1 0.0500 mol of a compound dissolves in water, causing the temperature of the solution to increase from 298 K to 301 K. The total mass of the solution is 220 g. Calculate the enthalpy change for the reaction in kJ mol^{-1}. Assume $c = 4.18 \text{ J g}^{-1} \text{ K}^{-1}$.

Q2 A calorimeter, containing 200 g of water ($c = 4.18 \text{ J g}^{-1} \text{ K}^{-1}$), was used to measure the enthalpy change of combustion of pentane ($C_5H_{12(l)}$, $M_r = 72.0$). 0.500 g of pentane was burnt, which increased the temperature of the water by 29.0 K.

a) Calculate the enthalpy change of combustion of pentane. Give your answer in kJ mol^{-1}.

b) Suggest reasons why this value may be different to the standard enthalpy change of combustion of pentane given in a data book.

Q3 The standard enthalpy of combustion of octane ($C_8H_{18(l)}$, $M_r = 114$) is $-5512 \text{ kJ mol}^{-1}$. Some octane was burnt in a calorimeter containing 300 g of water ($c = 4.18 \text{ J g}^{-1} \text{ K}^{-1}$). The temperature of the water went up by 55.0 K. Calculate an estimate of the mass of octane burnt.

Tip: If the temperature has increased during the reaction (i.e. it's exothermic), you need to use a negative value for q in your calculations.

Practice Questions — Fact Recall

Q1 What measurements need to be made in order to calculate the enthalpy change for a reaction in a laboratory?

Q2 Sketch and label a calorimeter that could be used in the lab to measure the enthalpy change of a combustion.

Q3 In the equation $q = mc\Delta T$, state what 'q' stands for and give its units.

Q4 What conditions are needed to measure the standard enthalpy change of a reaction, $\Delta_r H^{\circ}$?

Q5 Explain how you would calculate $\Delta_r H^{\circ}$ for a reaction, given a value for q and the number of moles, n, of a reactant used in the reaction.

4. Hess's Law

Learning Objective:

- Describe the techniques and procedures used to determine enthalpy changes indirectly.
- Use Hess' law to construct enthalpy cycles and carry out calculations to determine an enthalpy change of reaction, using either enthalpy changes of combustion, enthalpy changes of formation or an unfamiliar enthalpy cycle.

Specification Reference 3.2.1

For some reactions, there is no easy way to measure enthalpy changes in the lab. For these, we can use Hess's Law.

What is Hess's Law?

Hess's Law says that:

> The total enthalpy change of a reaction is always the same, no matter which route is taken.

This law is handy for working out enthalpy changes that you can't find directly by doing an experiment — for example, the enthalpy change of the reaction that breaks down NO_2 into N_2 and O_2. We can call this reaction 'route 1'. But we can also think of the reaction as NO_2 breaking down into NO and O_2, and then reacting further to form N_2 and O_2. This longer route, with an intermediate step, can be called 'route 2' (see Figure 1).

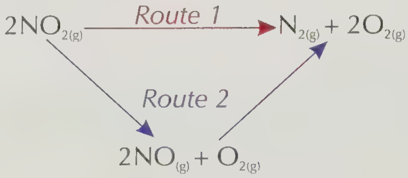


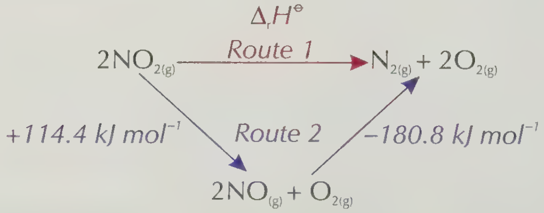
Figure 1: *Two possible routes for the formation of nitrogen and oxygen from nitrogen dioxide.*

Tip: It doesn't matter what you label as route 1 and route 2, or which routes you choose, the two routes will always be equal. It's just like magic — but less cool.

Hess's Law says that the total enthalpy change for route 1 is the same as for route 2. So if you know the enthalpy changes for the stages of route 2, you can calculate the enthalpy change for route 1, as shown in the example below.

Example — Maths Skills

Use Hess's Law to calculate the enthalpy change, $\Delta_r H^{\ominus}$, for route 1 of the reaction shown below.



The total enthalpy change for route 1 is the same as the total enthalpy change for route 2. So the enthalpy change for route 1 is the sum of the steps in route 2:

$\Delta_r H^{\ominus} = 114.4 \text{ kJ} + (-180.8 \text{ kJ}) = -66.4 \text{ kJ mol}^{-1}$.

Tip: As it says at the top of the page, you can't measure the enthalpy change for every reaction. So how did Hess prove that his Law worked? By building on already established theories — in this case, the principle of conservation of energy. Scientists knew that energy couldn't be created or destroyed, so if you start with the same reactants and end with the same products, it follows that the energy (or enthalpy) change has to be the same.

Using enthalpies of formation

You can find enthalpy changes of formation for hundreds of various compounds listed in data books. They're handy because you can use them (along with Hess's Law) to find enthalpy changes for all kinds of reactions.

You need to know $\Delta_f H^\circ$ for all the reactants and products that are compounds. The value of $\Delta_f H^\circ$ for elements is zero — the element's being formed from the element, so there's no change in enthalpy. The standard enthalpy changes are all measured at 298 K.

Examples — Maths Skills

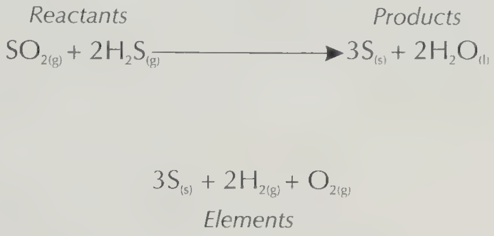
Calculate $\Delta_r H^\circ$ for this reaction using the enthalpies of formation in Figure 2:

$$SO_{2(g)} + 2H_2S_{(g)} \rightarrow 3S_{(s)} + 2H_2O_{(l)}$$

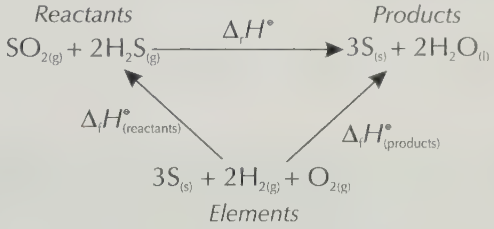
Compound	$\Delta_f H^\circ$
$SO_{2(g)}$	–297 kJ mol⁻¹
$H_2S_{(g)}$	–20.2 kJ mol⁻¹
$H_2O_{(l)}$	–286 kJ mol⁻¹

Figure 2: *Table of enthalpies of formation for three compounds.*

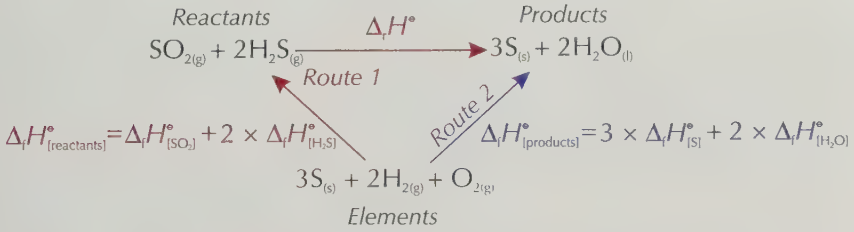
- Write under the reaction a list of all the elements present in the reaction, balanced in their correct molar quantities, as shown below:


Reactants
Products
$SO_{2(g)} + 2H_2S_{(g)}$
$3S_{(s)} + 2H_2O_{(l)}$
$3S_{(s)} + 2H_{2(g)} + O_{2(g)}$
Elements

- Enthalpies of formation ($\Delta_f H^\circ$) tell you the enthalpy change going from the elements to the compounds. The enthalpy change of reaction ($\Delta_r H^\circ$) is the enthalpy change going from the reactants to the products. Draw and label arrows to show this on your diagram:


Reactants
Products
$\Delta_r H^\circ$
$SO_{2(g)} + 2H_2S_{(g)}$
$3S_{(s)} + 2H_2O_{(l)}$
$\Delta_f H^\circ_{(reactants)}$
$\Delta_f H^\circ_{(products)}$
$3S_{(s)} + 2H_{2(g)} + O_{2(g)}$
Elements

- The calculation is often simpler if you keep the arrows end to end, so make both routes go from the elements to the products. Route 1 gets there via the reactants (and includes $\Delta_r H^\circ$), whilst route 2 gets there directly. Label the enthalpy changes along each arrow, as shown below. There are 2 moles of H_2O and 2 moles of H_2S, so their enthalpies of formation will need to be multiplied by 2. $\Delta_f H^\circ$ of sulfur is zero because it's an element, but you can still label it on the diagram.


Reactants
Products
$\Delta_r H^\circ$
$SO_{2(g)} + 2H_2S_{(g)}$
$3S_{(s)} + 2H_2O_{(l)}$
Route 1
Route 2
$\Delta_f H^\circ_{[reactants]} = \Delta_f H^\circ_{[SO_2]} + 2 \times \Delta_f H^\circ_{[H_2S]}$
$\Delta_f H^\circ_{[products]} = 3 \times \Delta_f H^\circ_{[S]} + 2 \times \Delta_f H^\circ_{[H_2O]}$
$3S_{(s)} + 2H_{2(g)} + O_{2(g)}$
Elements

Tip: You don't have to pick a route that follows the direction of the arrows. If your route goes against an arrow you can just change the signs (so negative enthalpies become positive and positive enthalpies become negative). There's an example of this on pages 177-178.

- Use Hess's Law, Route 1 = Route 2, and plug the numbers from Figure 2 into the equation:

$$\Delta_f H^\circ_{[SO_2]} + 2\Delta_f H^\circ_{[H_2S]} + \Delta_r H^\circ = 3\Delta_f H^\circ_{[S]} + 2\Delta_f H^\circ_{[H_2O]}$$

$$-297 + (2 \times -20.2) + \Delta_r H^\circ = (3 \times 0) + (2 \times -286)$$

$$\Delta_r H^\circ = [(3 \times 0) + (2 \times -286)] - [-297 + (2 \times -20.2)]$$

$$= -235 \text{ kJ mol}^{-1} \text{ (3 s.f.)}$$

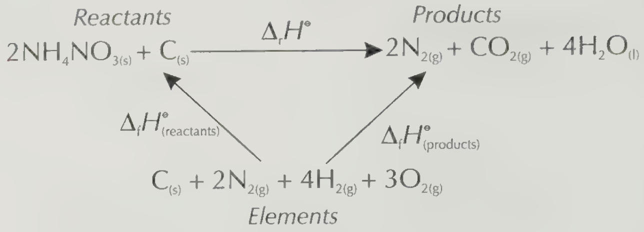
Compound	$\Delta_f H^\circ$
$NH_4NO_{3(s)}$	-365 kJ mol^{-1}
$CO_{2(g)}$	-394 kJ mol^{-1}
$H_2O_{(l)}$	-286 kJ mol^{-1}

Figure 3: *Table of enthalpies of formation for three compounds.*

Calculate $\Delta_r H^\circ$ for this reaction using the enthalpies of formation in Figure 3:

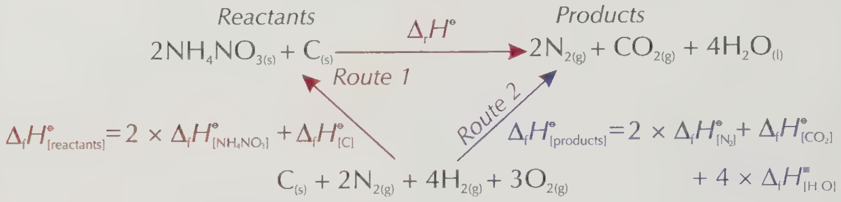
$$2NH_4NO_{3(s)} + C_{(s)} \rightarrow 2N_{2(g)} + CO_{2(g)} + 4H_2O_{(l)}$$

- Draw and label your diagram:



Reactants
Products
$\Delta_r H^\circ$
$2NH_4NO_{3(s)} + C_{(s)}$
$2N_{2(g)} + CO_{2(g)} + 4H_2O_{(l)}$
$\Delta_f H^\circ_{(reactants)}$
$\Delta_f H^\circ_{(products)}$
$C_{(s)} + 2N_{2(g)} + 4H_{2(g)} + 3O_{2(g)}$
Elements

- Label the enthalpy changes along each arrow.



Reactants
Products
$\Delta_r H^\circ$
$2NH_4NO_{3(s)} + C_{(s)}$
$2N_{2(g)} + CO_{2(g)} + 4H_2O_{(l)}$
Route 1
Route 2
$\Delta_f H^\circ_{[reactants]} = 2 \times \Delta_f H^\circ_{[NH_4NO_3]} + \Delta_f H^\circ_{[C]}$
$\Delta_f H^\circ_{[products]} = 2 \times \Delta_f H^\circ_{[N_2]} + \Delta_f H^\circ_{[CO_2]} + 4 \times \Delta_f H^\circ_{[H_2O]}$
$C_{(s)} + 2N_{2(g)} + 4H_{2(g)} + 3O_{2(g)}$

- Use Hess's Law, Route 1 = Route 2, and plug the numbers from Figure 3 into the equation:

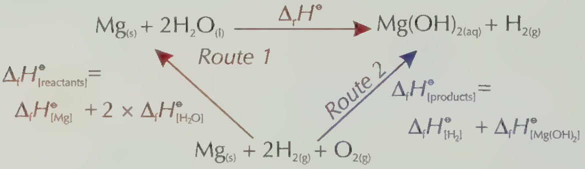
$$2\Delta_f H^\circ_{[NH_4NO_3]} + \Delta_f H^\circ_{[C]} + \Delta_r H^\circ = 2\Delta_f H^\circ_{[N_2]} + \Delta_f H^\circ_{[CO_2]} + 4\Delta_f H^\circ_{[H_2O]}$$
$$(2 \times -365) + 0 + \Delta_r H^\circ = 0 + -394 + (4 \times -286)$$
$$\Delta_r H^\circ = -394 + (-1144) - (-730) = -808 \text{ kJ mol}^{-1}.$$

Compound	$\Delta_f H^\circ$
$Mg(OH)_{2(s)}$	-925 kJ mol^{-1}
$H_2O_{(l)}$	-286 kJ mol^{-1}
$CO_{2(g)}$	-394 kJ mol^{-1}
$CaO_{(s)}$	-635 kJ mol^{-1}
$CaCO_{3(s)}$	-1207 kJ mol^{-1}
$N_2O_{5(s)}$	-41 kJ mol^{-1}
$NO_{2(g)}$	33 kJ mol^{-1}

Figure 4: *Table of enthalpies of formation for five compounds.*

Practice Questions — Application

Q1 Use Hess's Law and the diagram below to calculate $\Delta_r H^\circ$ for the reaction between magnesium and water. The enthalpies of formation needed are given in Figure 4.



$Mg_{(s)} + 2H_2O_{(l)}$
$\Delta_r H^\circ$
$Mg(OH)_{2(aq)} + H_{2(g)}$
Route 1
Route 2
$\Delta_f H^\circ_{[reactants]} =$
$\Delta_f H^\circ_{[Mg]} + 2 \times \Delta_f H^\circ_{[H_2O]}$
$\Delta_f H^\circ_{[products]} =$
$\Delta_f H^\circ_{[H_2]} + \Delta_f H^\circ_{[Mg(OH)_2]}$
$Mg_{(s)} + 2H_{2(g)} + O_{2(g)}$

Q2 Calculate $\Delta_r H^\circ$ for the following reactions using Hess's Law, and the enthalpies of formation given in Figure 4:

a) $CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}$

b) $2N_2O_{5(g)} \rightarrow 4NO_{2(g)} + O_{2(g)}$

Using enthalpies of combustion

You can use a similar method to find an enthalpy change from enthalpy changes of combustion, instead of using enthalpy changes of formation. There's a lovely example of this coming up on the next page...

Example — Maths Skills

Calculate $\Delta_f H^\circ$ of ethanol using the enthalpies of combustion in Figure 5.

Substance	$\Delta_c H^\circ$
$C_{(s)}$	–394 kJ mol^{-1}
$H_{2(g)}$	–286 kJ mol^{-1}
$C_2H_5OH_{(l)}$	–1367 kJ mol^{-1}

Figure 5: Table of enthalpies of combustion for three substances.

- The desired reaction in this case is the formation of ethanol from its elements, so write out the balanced equation:

Reactants *Product*

$$2C_{(s)} + 3H_{2(g)} + \tfrac{1}{2}O_{2(g)} \longrightarrow C_2H_5OH_{(l)}$$

- Figure 5 tells you the enthalpy change when each of the 'reactants' and 'products' is burned in oxygen. Add these combustion reactions to your diagram, making sure they are balanced, as shown below:

Reactants *Product*

$$\begin{tikzcd}
2C_{(s)} + 3H_{2(g)} + \tfrac{1}{2}O_{2(g)} \arrow[rr] \arrow[dr, "+3O_{2(g)}"'] & & C_2H_5OH_{(l)} \arrow[dl, "+3O_{2(g)}"] \\
& 2CO_{2(s)} + 3H_2O_{(l)} &
\end{tikzcd}$$

Combustion products

- Choose which reactions will form which route. Label the diagram with the enthalpy changes along each arrow as before (taking into account molar quantities):

Reactants *Product*

$$\begin{tikzcd}
2C_{(s)} + 3H_{2(g)} + \tfrac{1}{2}O_{2(g)} \arrow[rr, "\Delta_f H^\circ"] \arrow[dr, "+3O_{2(g)}"', "\text{Route 2}"] \arrow[dr, phantom, "\Delta_c H^\circ_{[\text{reactants}]} = 2 \times \Delta_c H^\circ_{[C]} + 3 \times \Delta_c H^\circ_{[H_2]}"', shift right=6] & & C_2H_5OH_{(l)} \arrow[dl, "+3O_{2(g)}", "\Delta_c H^\circ_{[C_2H_5OH]}"'] \arrow[ll, phantom, "\text{Route 1}"', shift right=3] \\
& 2CO_{2(s)} + 3H_2O_{(l)} &
\end{tikzcd}$$

Combustion products

- Use Hess's Law as follows: Route 1 = Route 2

$$\Delta_f H^\circ_{[\text{ethanol}]} + \Delta_c H^\circ_{[C_2H_5OH]} = 2\Delta_c H^\circ_{[C]} + 3\Delta H^\circ_{c\ [H_2]}$$
$$\Delta_f H^\circ_{[\text{ethanol}]} + (-1367) = (2 \times -394) + (3 \times -286)$$
$$\Delta_f H^\circ_{[\text{ethanol}]} = -788 + -858 - (-1367) = -279 \text{ kJ mol}^{-1}.$$

Tip: The products of a complete combustion of a CHO compound in oxygen are carbon dioxide (CO_2) and water (H_2O).

Tip: You can ignore the enthalpy change of combustion of oxygen in these calculations. Oxygen doesn't have an enthalpy change of combustion — you can't burn 1 mole of oxygen in oxygen.

Using enthalpies of reaction

You can also use Hess's Law to calculate enthalpy changes using a group of linked reactions, where all but one of the enthalpy changes for the reactions are known. The following example shows how to do this, this time choosing routes where the arrows don't run end to end.

Reaction	$\Delta_r H^\circ$
ΔH_1	+987 kJ mol^{-1}
ΔH_2	–366 kJ mol^{-1}
ΔH_3	–85 kJ mol^{-1}

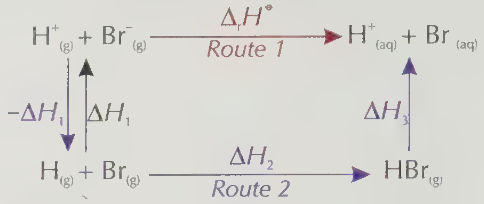
Figure 6: Table of enthalpies of reaction for three reactions.

Example — Maths Skills

Calculate $\Delta_r H^\circ$ for the reaction below using the data given in Figure 6.

$$\begin{tikzcd}
H^+_{(g)} + Br^-_{(g)} \arrow[r, "\Delta_r H^\circ"] & H^+_{(aq)} + Br^-_{(aq)} \\
H_{(g)} + Br_{(g)} \arrow[u, "\Delta H_1"'] \arrow[r, "\Delta H_2"] & HBr_{(g)} \arrow[u, "\Delta H_3"]
\end{tikzcd}$$

You are given three of the four enthalpies for these reactions, so use Hess's Law to find the unknown $\Delta_r H^\circ$. First though, choose and label the two routes. For this example we will choose routes that go against the direction of the arrows, to show how this method works:



The first step in the chosen route 2 goes against the direction of the arrow for ΔH_1. The enthalpy change for a backwards reaction is exactly the same size as for the forwards reaction — but with the opposite sign. So the enthalpy change for the first step in route 2 will be $-\Delta H_1$, as shown.

Now just use Hess's Law as before:

Route 1 = Route 2

$\Delta_r H^\circ = -\Delta H_1 + \Delta H_2 + \Delta H_3$

$\Delta_r H^\circ = -987 + (-366) + (-85) = -1438$ kJ mol^{-1}.

Exam Tip
It doesn't really matter how you pick your routes to do the Hess's Law calculation in an exam question, so choose a method that you're comfortable with. Just take care with the positives and negatives by labelling everything clearly and writing down each step of your working.

Element	$\Delta_c H^\circ$
$C_{(s)}$	–394 kJ mol^{-1}
$H_{2(g)}$	–286 kJ mol^{-1}

Figure 7: Enthalpies of combustion for carbon and hydrogen.

Practice Questions — Application

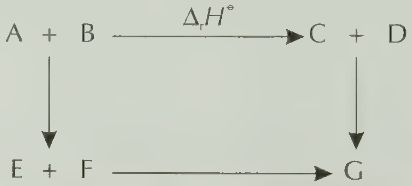
Q1 Calculate $\Delta_f H^\circ$ for the following organic compounds using Hess's Law, and the enthalpies of combustion given in Figure 7 and below:

a) propan-1-ol (C_3H_7OH): $\Delta_c H^\circ = -2021$ kJ mol^{-1}.

b) ethane-1,2-diol ($C_2H_4(OH)_2$): $\Delta_c H^\circ = -1180$ kJ mol^{-1}.

c) butan-2-one (C_4H_8O): $\Delta_c H^\circ = -2442$ kJ mol^{-1}.

Q2 The reaction scheme below involves 7 unknown substances, A-G:



Reaction	ΔH (kJ mol^{-1})
A + B → E + F	–837
E + F → G	+89
C + D → G	+424

Use Hess's Law, along with the data in the table, to calculate the enthalpy change, $\Delta_r H^\circ$, for the reaction A + B → C + D.

5. Reaction Rates

The rate of a reaction is how quickly the reaction happens.

Learning Objectives:

- Explain qualitatively the Boltzmann distribution and its relationship with activation energy.
- Explain qualitatively, using the Boltzmann distribution, the effect of temperature changes on the proportion of molecules exceeding the activation energy and hence the reaction rate.
- Describe qualitatively, in terms of frequency of collisions, the effect of concentration changes on the rate of a reaction.
- Describe qualitatively, in terms of frequency of collisions, the effect of pressure changes in gases on the rate of a reaction.

Specification Reference 3.2.2

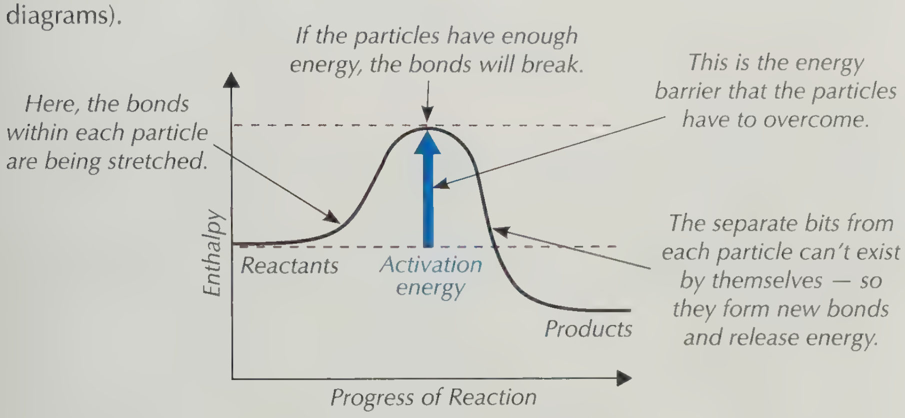
Collision theory and activation energy

Particles in liquids and gases are always moving and colliding with each other. They don't react every time though — only when the conditions are right. **Collision theory** says that a reaction won't take place between two particles unless they collide in the right direction (they need to be facing each other the right way) and they collide with at least a certain minimum amount of kinetic (movement) energy.

The minimum amount of kinetic energy particles need to react is called the **activation energy**. The particles need this much energy to break the bonds to start the reaction. Reactions with low activation energies often happen pretty easily. But reactions with high activation energies don't. You need to give the particles extra energy by heating them.

Enthalpy profile diagrams

To make things a bit clearer, we can draw an enthalpy profile diagram like the one shown below in Figure 1 (see page 167 for more on enthalpy profile diagrams).


If the particles have enough energy, the bonds will break.

Here, the bonds within each particle are being stretched.

This is the energy barrier that the particles have to overcome.

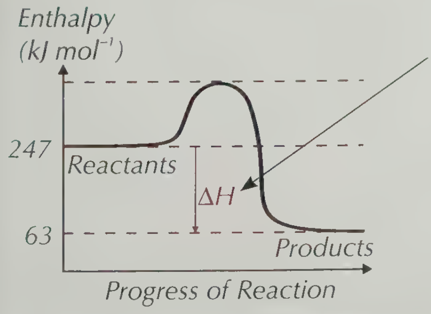
The separate bits from each particle can't exist by themselves — so they form new bonds and release energy.

***Figure 1:** An enthalpy profile diagram.*

Enthalpy profile diagrams can be used to work out the enthalpy change (ΔH) of a reaction, and whether it is exothermic or endothermic (see pages 166-167). ΔH is the difference between the enthalpy of the reactants and the enthalpy of the products on the diagram. If the products have a lower enthalpy than the reactants, the reaction is exothermic. If the products have a higher enthalpy than the reactants, the reaction is endothermic.

Tip: Remember, for exothermic reactions ΔH is negative. For endothermic reactions, ΔH is positive.

Example



ΔH = enthalpy of products − enthalpy of reactants

$\Delta H = 63 - 247 = -184$ kJ mol^{-1}.

ΔH is negative, and the graph shows that the products are at a lower enthalpy than the reactants — so, the reaction is exothermic.

Figure 2: Ludwig Boltzmann, the Austrian physicist who developed the ideas on the energy distribution of gas molecules.

Tip: In science, it's important to be able to look at theoretical models and use the ideas behind them to explain the results of experiments.

Boltzmann distributions

Imagine looking down on Oxford Street when it's teeming with people. You'll see some people ambling along slowly, some hurrying quickly, but most of them will be walking with a moderate speed. It's the same with the molecules in a liquid or gas. Some don't have much kinetic energy and move slowly. Others have loads of kinetic energy and whizz along. But most molecules are somewhere in between. If you plot a graph of the numbers of molecules in a substance with different kinetic energies you get a **Boltzmann distribution**. The Boltzmann distribution is a theoretical model that has been developed to explain scientific observations (see page 1). It looks like this:

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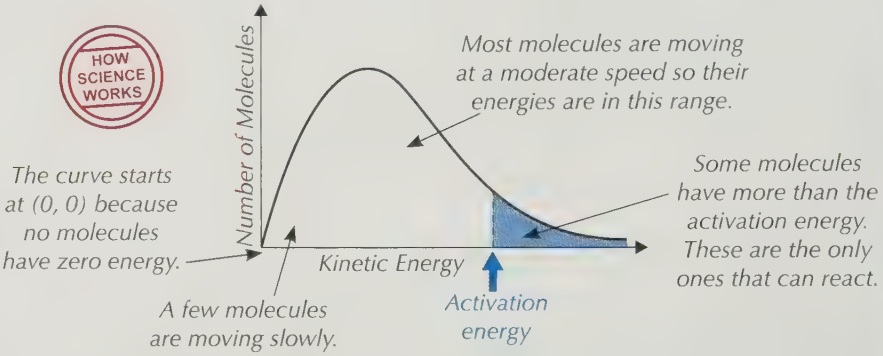


Figure 3: A Boltzmann distribution curve showing the different kinetic energies of molecules in a gas.

The effect of temperature on reaction rate

If you increase the temperature of a substance, the molecules will, on average, have more kinetic energy and will move faster. So, a greater proportion of molecules will have at least the activation energy and be able to react. This changes the shape of the Boltzmann distribution curve — it pushes it over to the right (see Figure 4). The total number of molecules is still the same, which means the area under each curve must be the same.

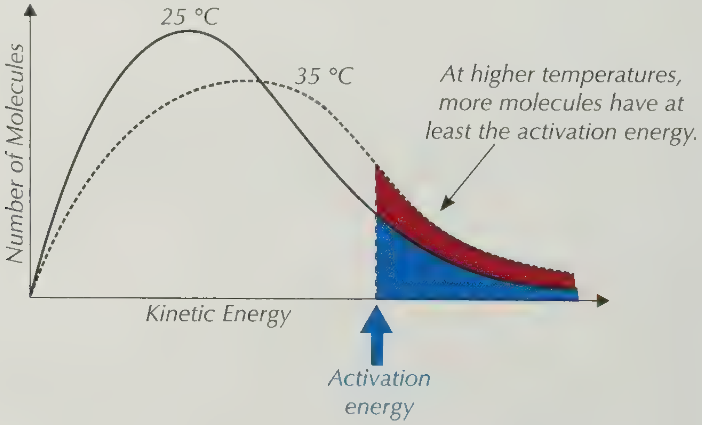


Figure 4: Two Boltzmann distribution curves for a gas at different temperatures. Increasing the temperature of the gas shifts the distribution of the kinetic energies of the molecules.

Because the molecules are flying about faster, they'll collide more often. This is another reason why increasing the temperature makes a reaction faster. So, small temperature increases can lead to large increases in reaction rate.

Exam Tip
You need to be able to draw distribution curves for different temperatures so remember — if the temperature increases the curve moves to the right, if it decreases the curve moves to the left.

Exam Tip
When drawing Boltzmann distribution curves, make sure your line starts at the origin, but doesn't end touching the x-axis.

The effect of concentration on reaction rate

If you increase the concentration of reactants in a solution, the particles will on average be closer together. If they're closer, they'll collide more often. If there are more collisions, they'll have more chances to react.

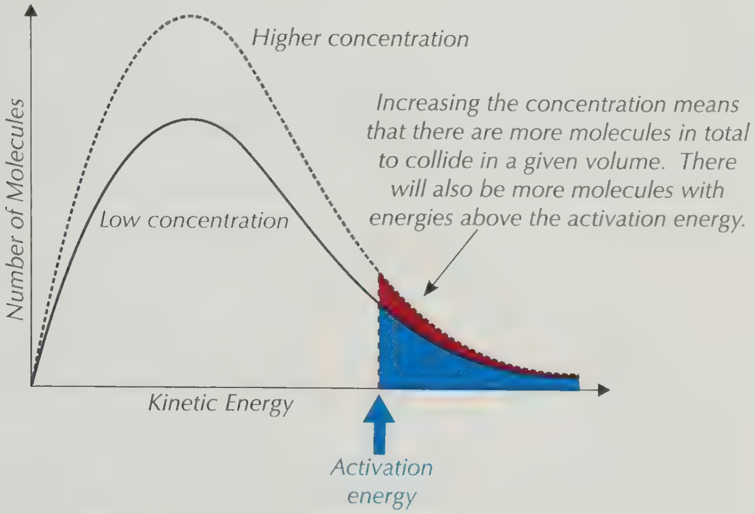


Figure 5: *Two Boltzmann distribution curves for a solution at different concentrations.*

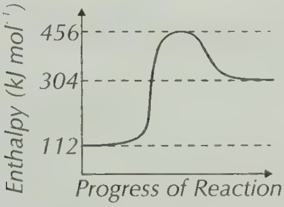
Tip: Figure 5 refers to the number of molecules in a given volume. Changing the volume as well as the concentration means that two variables in the experiment have changed — you wouldn't be able to tell what was causing the change in the Boltzmann distribution. See page 5 for more on variables.

If any of your reactants are gases, increasing the pressure will increase the rate of reaction. It's pretty much the same as increasing the concentration of a solution — at higher pressures, the particles will be closer together, increasing the chance of collisions. As a result there'll be more successful collisions.

Tip: If one of the reactants is a solid, increasing its surface area makes the reaction faster too.

Practice Questions — Application

Q1 Look at the enthalpy profile diagram below.



Is the reaction exothermic or endothermic? Explain your answer.

Q2 The two Boltzmann distribution curves shown in Figure 6 are for the same volume of the same gas. Which curve, A or B, is for the gas at a higher temperature? Explain your answer.

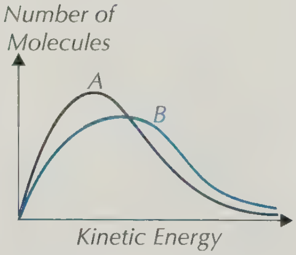


Figure 6: *Two Boltzmann distribution curves for a volume of gas at different temperatures.*

Practice Questions — Fact Recall

Q1 What conditions are required for a collision between two particles to result in a reaction?

Q2 What does the term 'activation energy' mean?

Q3 Explain why a small increase in temperature can lead to a large increase in reaction rate.

Q4 Describe and explain the effect that increasing the concentration of a solution has on the rate of a reaction involving that solution.

Learning Objectives:

- Explain the role of a catalyst in increasing reaction rate without being used up by the overall reaction.
- Explain the role of a catalyst in allowing a reaction to proceed via a different route with lower activation energy, as shown by enthalpy profile diagrams.
- Interpret catalytic behaviour in terms of the Boltzmann distribution.
- Know that a heterogeneous catalyst is in a different phase to the reactants and that a homogeneous catalyst is in the same phase as the reactants.
- Explain that catalysts have great economic importance.
- Explain the benefits of using catalysts for increased sustainability by lowering temperatures and reducing energy demand from combustion of fossil fuels with resulting reduction in CO_2 emissions.

Specification Reference 3.2.2

6. Catalysts

Sometimes you need to speed up a reaction, but you can't (or don't want to) increase the temperature, concentration or pressure any further. That's where catalysts come in.

What is a catalyst?

You can use **catalysts** to make chemical reactions happen faster. A catalyst increases the rate of a reaction by providing an alternative reaction pathway with a lower activation energy. The catalyst is chemically unchanged at the end of the reaction.

Catalysts are great. They don't get used up in reactions, so you only need a tiny bit of catalyst to catalyse a huge amount of stuff. They do take part in reactions, but they're remade at the end. Catalysts are very fussy about which reactions they catalyse. Many will usually only work on a single reaction. Catalysts save heaps of money in industrial processes.

Example

The Haber-Bosch process uses an iron catalyst to increase the rate of forming ammonia from nitrogen and hydrogen in the following reaction:

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

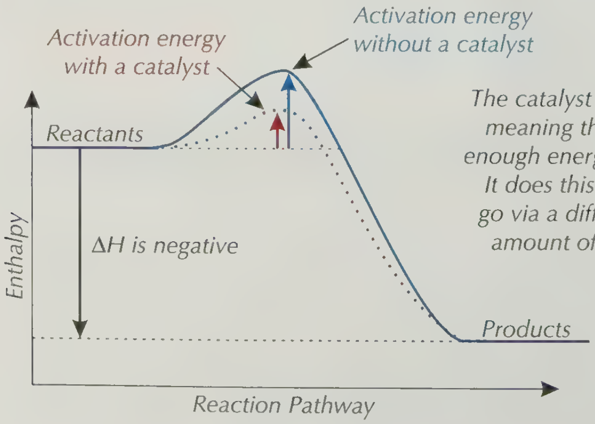
This reaction has a very high activation energy, due to a very strong N≡N bond in N_2. For the reaction rate to be high enough to make ammonia in any great quantity, the temperature and pressure would have to be extremely high — too high to be practical or profitable.

In reality, the reaction is performed with the use of an iron catalyst, which increases the reaction rate at a workable temperature and pressure (around 400-500 °C and 20 MPa).

How do catalysts work?

When a suitable catalyst is present in a reaction, the reactant molecules bind to the catalyst. This makes it easier to break the bonds, and so the activation energy of the reaction decreases. The broken reactant molecules then form product molecules, and break away from the catalyst.

Enthalpy profiles (see Figure 1) and Boltzmann distribution curves (Figure 2 — next page) can help illustrate how catalysts work.



The catalyst lowers the activation energy, meaning there are more particles with enough energy to react when they collide. It does this by allowing the reaction to go via a different route. So, in a certain amount of time, more particles react.

Figure 1: *Enthalpy profile diagram for a reaction with and without a catalyst.*

With a catalyst present, the molecules still have the same amount of energy, so the Boltzmann distribution curve is unchanged. But because the catalyst lowers the activation energy, more of the molecules have energies above this threshold and are able to react, as shown in Figure 2.

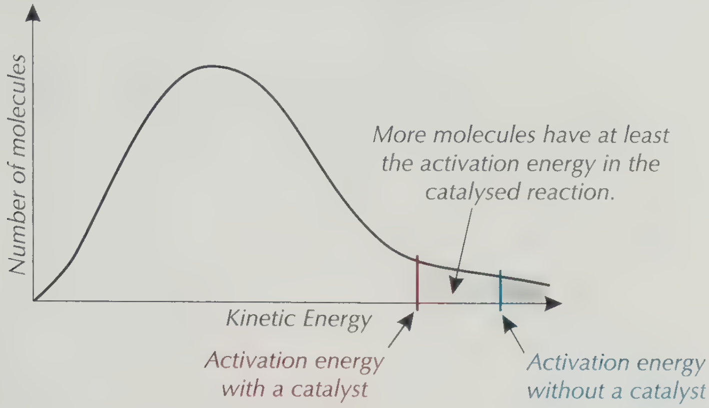


***Figure 2:** A Boltzmann distribution curve for a reaction with and without a catalyst.*

Tip: Catalysts speed up the reaction in a different way to increasing temperature, concentration or pressure. These things all change the energy distribution but the addition of a catalyst does not.

Homogeneous and heterogeneous catalysts

A **heterogeneous** catalyst is one that is in a different phase from the reactants — i.e. in a different physical state. For example, in the Haber Process (see the previous page), gases are passed over a solid iron catalyst. The reaction happens on the surface of the heterogeneous catalyst. So, increasing the surface area of the catalyst increases the number of molecules that can react at the same time, increasing the rate of the reaction.

Homogeneous catalysts are in the same physical state as the reactants. Usually a homogeneous catalyst is an aqueous catalyst for a reaction between two aqueous solutions. A homogeneous catalyst works by forming an intermediate species. One or more reactants combine with the catalyst to make the intermediate species, which then reacts to form the products and reform the catalyst.

Catalysts in industry

Loads of industries rely on catalysts. They can dramatically lower production costs, and help make better products.

Examples

Using a catalyst changes the properties of poly(ethene).

	Made without a catalyst	Made with a catalyst (a Ziegler-Natta catalyst to be precise)
Properties of poly(ethene)	▪ less dense ▪ less rigid	▪ more dense ▪ more rigid ▪ higher melting point

***Figure 3:** A table showing the properties of poly(ethene) made with and without a Ziegler-Natta catalyst.*

Iron is used as a catalyst in ammonia production (see page 182).

Tip: Interesting fact — the chemists Karl Ziegler and Giulio Natta shared the Nobel Prize for chemistry in 1963 for their work developing the Ziegler-Natta catalyst. Fascinating.

Catalysts and the environment

Using catalysts means that lower temperatures and pressures can be used. So energy is saved, meaning less CO_2 is released, and fossil fuel reserves are preserved. They can also reduce waste by allowing a different reaction to be used with a better atom economy. (See page 92 for more on atom economy.)

Example

Making the painkiller ibuprofen by the traditional method involves 6 steps and has an atom economy of 32%. Using catalysts, it can be made in 3 steps with an atom economy of 77%.

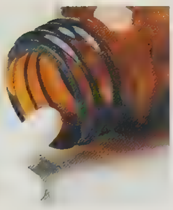


Figure 4: Tablets of the painkiller ibuprofen.

Catalytic converters on cars are made from alloys of platinum, palladium and rhodium. They reduce the pollution released into the atmosphere by speeding up the following reaction:

$$2CO + 2NO \rightarrow 2CO_2 + N_2$$

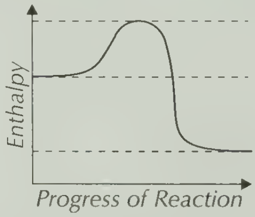
HOW SCIENCE WORKS

But catalysts don't last forever. All catalysts eventually need to be disposed of. The trouble is, many contain nasty toxic compounds, which may leach into the soil if they're sent directly to landfill. So it's important to try to recycle them, or convert them to non-leaching forms. If catalysts contain valuable metals, such as platinum, it's worth recovering and recycling it — and there are special companies eager to do this. The decision whether to recycle the catalyst or to send it to landfill is made by balancing the economic and environmental factors.

Tip: 'Uncatalysed' just means that no catalyst has been used.

Practice Question — Application

Q1 The enthalpy profile diagram shown below is for an uncatalysed chemical reaction to produce 'Product X'.



A company wants to produce 'Product X' on a large scale. They are considering using a catalyst.

a) Draw a sketch to show how the addition of a catalyst would affect the enthalpy profile diagram for the reaction.

b) The uncatalysed reaction will only take place at temperatures above 1000 °C. Suggest how adding a catalyst would improve the industrial process.

Exam Tip
You need to be able to give a full description of what a catalyst is.

Practice Questions — Fact Recall

Q1 What is a catalyst?

Q2 Explain why catalysts are used in many industrial processes.

Q3 Explain how a catalyst can speed up the rate of a reaction.

Q4 What's the difference between homogeneous and heterogeneous catalysts?

7. Calculating Reaction Rates

Understanding all about the rates of chemical reactions is a really important part of chemistry. You've already learnt a bit about reaction rates, but now it's time to cover things in a bit more detail.

Learning Objectives:

- Know about the techniques and procedures used to investigate reaction rates, including the measurement of mass, gas volume and time.
- Calculate reaction rates from the gradients of graphs measuring how a physical quantity changes over time.
- Measurement of rate of reaction by continuous monitoring methods (PAG 9).

Specification Reference 3.2.2

What are reaction rates?

The **reaction rate** is how fast a reaction takes place. It is defined as the change in the amount of reactants or products per unit time (normally per second). The units for the rate of a reaction will be 'what you're measuring per unit of time'. E.g. g s^{-1} or cm^3 s^{-1}:

$$\text{rate of reaction} = \frac{\text{amount of reactant used or product formed}}{\text{time}}$$

Measuring the progress of a reaction

If you want to find the rate of a reaction, you need to be able to follow the reaction as it's occurring. Although there are quite a few ways to follow reactions, not every method works for every reaction. You've got to pick a property that changes as the reaction goes on. Here are a few examples:

Change in mass

When the product is a gas, its formation can be measured using a mass balance.

PRACTICAL ACTIVITY GROUP 9

Example

This would work for the reaction between an acid and a carbonate in which carbon dioxide gas is given off.

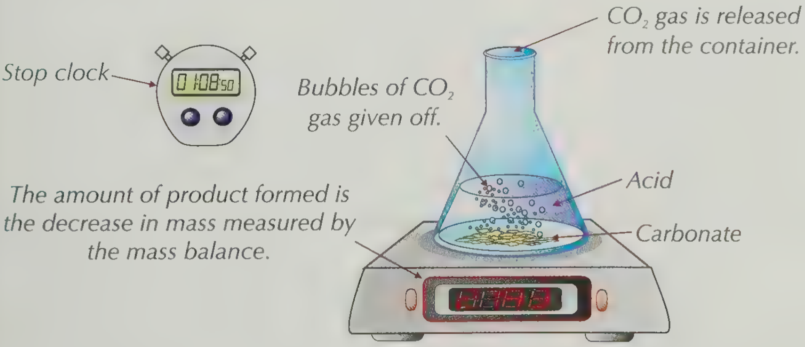

CO_2 gas is released from the container.
Stop clock
Bubbles of CO_2 gas given off.
Acid
The amount of product formed is the decrease in mass measured by the mass balance.
Carbonate

Figure 1: *Experimental set-up for measuring the reaction rate by monitoring the change in mass of a reaction mixture.*

When the reaction starts, you should start a stop clock or timer. Then take mass measurements at regular time intervals. Make a table with a column for 'time' and a column for 'mass' and fill it in as the reaction goes on (see Figure 2). You'll know the reaction is finished when the reading on the mass balance stops decreasing. This method is very accurate and easy to use but does release gas into the room, which could be dangerous if the gas is toxic or flammable. So it's best to carry out the experiment in a fume cupboard.

Time (s)	Mass (g)
0	280.0
30	279.3
60	278.7
90	278.2
120	278.0
150	277.9
180	277.8
210	277.7
240	277.7
270	277.7

Figure 2: *Results of the experiment carried out in Figure 1.*

Tip: Acids can be dangerous and releasing gases into the lab (even in a fume cupboard) is potentially hazardous, so make sure you carry out a risk assessment before carrying out these experiments.

Gas volume

PRACTICAL ACTIVITY GROUP 9

If a gas is given off, you could collect it in a gas syringe and record how much you've got at regular time intervals.

Example

This would work for the reaction between magnesium and an acid in which hydrogen gas is given off.

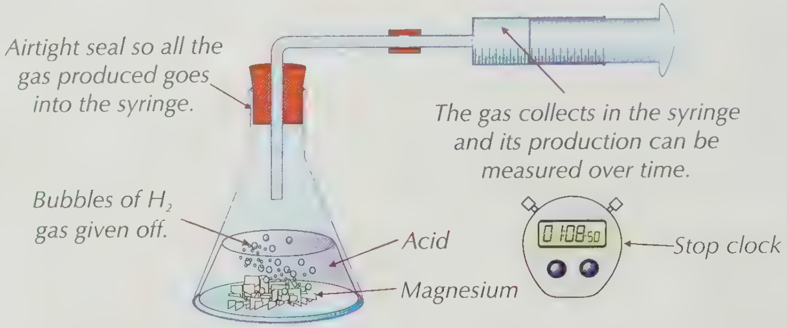

Airtight seal so all the gas produced goes into the syringe.
The gas collects in the syringe and its production can be measured over time.
Bubbles of H_2 gas given off.
Acid
Magnesium
0 108 50
Stop clock

Figure 3: *Experimental set-up for measuring the reaction rate by monitoring the volume of gas given off by a reaction mixture.*

The experiment is carried out in a similar way as when measuring the change in mass but this time you're measuring the volume of the gas in the syringe rather than the mass from the balance (see Figure 4). This method is accurate but vigorous reactions can blow the plunger out of the syringe. Because no gas escapes, this method can be used for toxic or flammable gases.

Time (s)	Volume (cm^3)
0	0.0
30	6.1
60	10.9
90	15.2
120	17.7
150	20.0
180	21.1
210	21.9
240	22.0
270	22.0

Figure 4: *Results of the experiment carried out in Figure 3.*

Other methods

There are a few other ways to measure the amount of reactant used or product formed. For example, you can monitor changes in pressure (for gases), changes in colour (for solutions) or changes in conductivity. The best method depends on the reaction you're looking at.

Tip: The rate of reaction slows down as time progresses. This is because the reactants get used up, and so collisions between reactant molecules become less likely.

Working out reaction rates

If you draw a graph where the *x*-axis is time and the *y*-axis is a measure of either the amount of reactant or product, then the reaction rate is just the gradient of the graph. If the graph's a curve, you have to draw a **tangent** to the curve and find the gradient of that. A tangent is a line that just touches a curve and has the same gradient as the curve does at that point. Figure 5 shows how a graph of the mass of a reaction vessel against time might look.

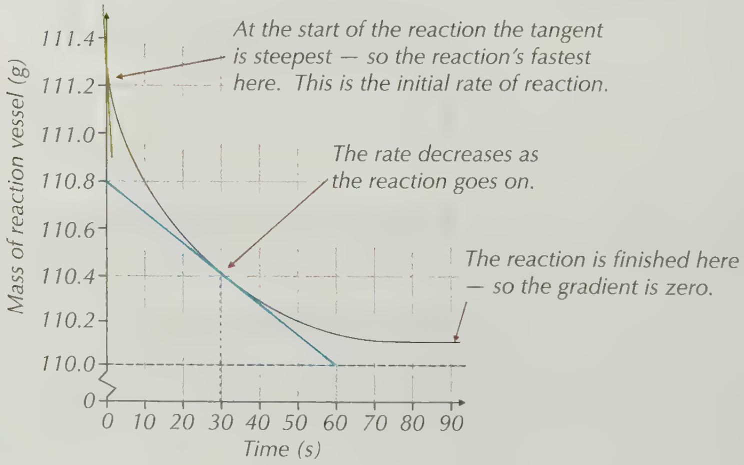
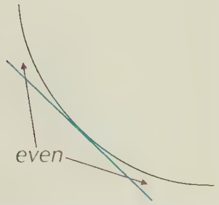


Figure 5: *Graph showing the mass of a reaction vessel against time.*

Tip: When you're drawing a tangent, try to do it so that the gaps between the graph line and the tangent on either side of the point are as even as possible. i.e.

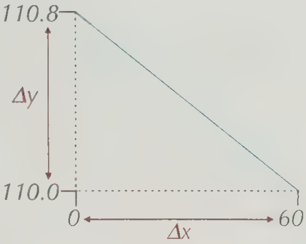


The gradient of a tangent is the change in vertical height (Δ*y*) divided by the change in horizontal width (Δ*x*).

Tip: Don't forget, the *x*-axis is the horizontal axis and the *y*-axis is the vertical axis.

Example — **Maths Skills**

On the mass-time graph in Figure 5, the gradient of the blue tangent is the rate of reaction at 30 seconds. This tangent makes a triangle. The change in *y* is –0.8 and the change in *x* is 60, so:



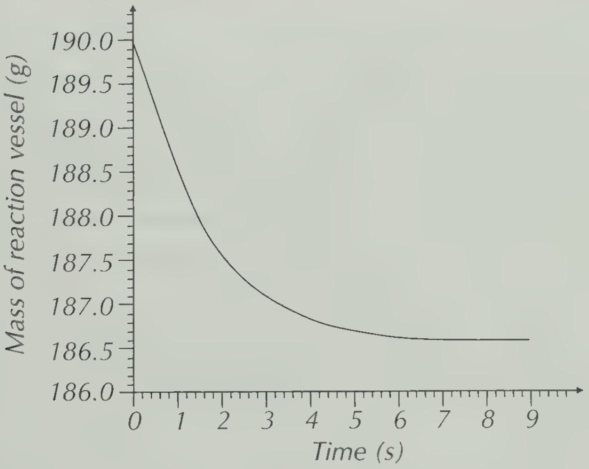
$$\text{Gradient} = \frac{\Delta y}{\Delta x} = \frac{-0.8}{60} = -0.013 \text{ g s}^{-1}$$

This means that the rate of reaction at 30 seconds is 0.013 g s^{-1}.

In this context, the sign of the gradient doesn't really matter — it's a negative gradient when you're measuring the mass of a reaction vessel because the reactant decreases. If you measured the volume of gas produced, it'd be a positive gradient.

Practice Question — Application

Q1 The mass-time graph for a reaction is shown below:



Exam Tip
Don't be afraid to draw on the graphs you're given in the exam — you'll need to draw tangents to find the gradients of curves.

Determine the rate of this reaction after:

a) 1 second,

b) 2 seconds,

c) 4 seconds.

Practice Questions — Fact Recall

Q1 What is a reaction rate?

Q2 Give an example of a unit of reaction rate.

Q3 Suggest two ways in which the progress of a reaction could be measured.

Q4 a) Describe the experimental procedure used to produce a mass-time graph for a reaction.

b) Explain how you could determine the rate of a reaction at a particular time using a mass-time graph.

8. Reversible Reactions

We usually think of a reaction as a one-way process to make products from reactants. In reality though, many reactions are reversible.

Learning Objectives:

- Explain that a dynamic equilibrium exists in a closed system when the rate of the forward reaction is equal to the rate of the reverse reaction and the concentrations of reactants and products do not change.
- Be able to apply Le Chatelier's principle to deduce qualitatively (from appropriate information) the effect of a change in temperature, concentration or pressure, on the position of equilibrium in a homogeneous system in equilibrium.
- Explain that a catalyst increases the rate of both forward and reverse reactions in an equilibrium by the same amount, resulting in an unchanged equilibrium position.
- Be able to explain the importance in the chemical industry of a compromise between chemical equilibrium and reaction rate in deciding the operational conditions.
- Describe the techniques and procedures used to investigate changes to the position of equilibrium for changes in concentration and temperature.

Specification Reference 3.2.3

Dynamic equilibrium

Lots of chemical reactions are reversible — they go both ways. To show a reaction's reversible, you stick in a $\rightleftharpoons$.

Example

Hydrogen will react with iodine to produce hydrogen iodide:

$$\mathbf{H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}}$$

This reaction can go in either direction —

forwards: $H_{2(g)} + I_{2(g)} \rightarrow 2HI_{(g)}$ ...or backwards: $2HI_{(g)} \rightarrow H_{2(g)} + I_{2(g)}$

As the reactants get used up, the forward reaction slows down — and as more product is formed, the reverse reaction speeds up. After a while, the forward reaction will be going at exactly the same rate as the backward reaction so the concentration of reactants and products won't be changing any more — it'll seem like nothing's happening. It's a bit like you're digging a hole while someone else is filling it in at exactly the same speed. This is called a **dynamic equilibrium**. At equilibrium, the concentrations of reactants and products stay constant. A dynamic equilibrium can only happen in a **closed system**. This just means nothing can get in or out.

Le Chatelier's principle

If you change the concentration, pressure or temperature of a reversible reaction, you're going to alter the position of equilibrium. This just means you'll end up with different amounts of reactants and products at equilibrium. If the position of equilibrium moves to the left, the backwards reaction is faster than the forwards reaction, and so you'll get more reactants.

Example

If the position of equilibrium in the reaction $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$ shifts to the left, the backwards reaction is fastest, so more H_2 and I_2 are produced:

$$\mathbf{H_{2(g)} + I_{2(g)} \leftrightharpoons 2HI_{(g)}}$$

If the position of equilibrium moves to the right, the forwards reaction is faster than the backwards reaction, and so you'll get more products.

Example

If the position of equilibrium in the reaction $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$ shifts to the right, the forwards reaction is fastest, so more HI is produced:

$$\mathbf{H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}}$$

Le Chatelier's principle tells you how the position of equilibrium will change if a condition changes:

> If there's a change in concentration, pressure or temperature, the equilibrium will move to help counteract the change.

So, basically, if you raise the temperature, the position of equilibrium will shift to try to cool things down. And, if you raise the pressure or concentration, the position of equilibrium will shift to try to reduce it again. Catalysts have no effect on the position of equilibrium.

Using Le Chatelier's principle

Changing concentration

If you increase the concentration of a reactant, the equilibrium tries to get rid of the extra reactant. It does this by making more product. So the equilibrium's shifted to the right. If you increase the concentration of the product, the equilibrium tries to remove the extra product. This makes the reverse reaction go faster. So the equilibrium shifts to the left. Decreasing the concentrations has the opposite effect.

Examples

Sulfur dioxide reacts with oxygen to produce sulfur trioxide:

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

If you increase the concentration of SO_2 or O_2, the equilibrium tries to get rid of it by making more SO_3, so the equilibrium shifts to the right. If you increase the concentration of SO_3, the equilibrium shifts to the left to make the backwards reaction faster to get rid of the extra SO_3.

In the Haber process, nitrogen reacts with hydrogen to produce ammonia:

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

If you increase the concentration of N_2 or H_2, the equilibrium shifts to the right and you'll make more NH_3. If you increase the concentration of NH_3, the equilibrium shifts to the left and you'll make more N_2 and H_2.

Figure 1: *Henri Le Chatelier, the French physical chemist who developed Le Chatelier's principle in the 1880s.*

Changing pressure

Changing the pressure only affects equilibria involving gases. Increasing the pressure shifts the equilibrium to the side with fewer gas molecules. This reduces the pressure. Decreasing the pressure shifts the equilibrium to the side with more gas molecules. This raises the pressure again.

Examples

When sulfur dioxide reacts with oxygen you get sulfur trioxide:

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

There are 3 moles on the left, but only 2 on the right. So, an increase in pressure shifts the equilibrium to the right, making more SO_3 and reducing the pressure. Decreasing the pressure favours the backwards reaction, so the equilibrium shifts to the left and more SO_2 and O_2 will be made to increase the pressure.

Methane reacts with steam to produce carbon monoxide and hydrogen:

$$CH_{4(g)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + 3H_{2(g)}$$

There are 2 moles on the left and 4 on the right. So for this reaction an increase in pressure shifts the equilibrium to the left, making more CH_4 and H_2O. Decreasing the pressure shifts the equilibrium to the right to make more CO and H_2. This reaction is used in industry to produce hydrogen. It is best performed at a low pressure to favour the forwards reaction so that more H_2 is produced.

Tip: If there are the same number of moles of gas on each side of the equation, changing the pressure won't change the position of equilibrium.

Changing temperature

Increasing the temperature means adding heat energy. The equilibrium shifts in the endothermic (positive ΔH) direction to absorb this energy. Decreasing the temperature removes heat energy. The equilibrium shifts in the exothermic (negative ΔH) direction to try to replace the heat energy. If the forward reaction is endothermic, the reverse reaction will be exothermic, and vice versa.

Tip: An enthalpy change given with a reversible reaction always refers to the forwards reaction, unless you're told otherwise.

Exam Tip
In an exam question, make it clear exactly how the equilibrium shift opposes a temperature change — i.e. by removing or producing heat.

Examples

This reaction's exothermic in the forward direction, which means it is endothermic in the backward direction.

$$\underset{\leftarrow Endothermic}{\overset{Exothermic\rightarrow}{2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}}} \quad \Delta H = -197 \text{ kJ mol}^{-1}.$$

If you increase the temperature, the equilibrium shifts to the left (the endothermic direction) to absorb the extra heat. This means more SO_2 and O_2 are produced. If you decrease the temperature, the equilibrium shifts to the right (the exothermic direction) to produce more heat. This means more SO_3 is produced.

This reaction's endothermic in the forward direction (and so exothermic in the backward direction).

$$\underset{\leftarrow Exothermic}{\overset{Endothermic\rightarrow}{C_{(s)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + H_{2(g)}}} \qquad \Delta H = +131 \text{ kJ mol}^{-1}.$$

Increasing the temperature will shift the equilibrium to the right, producing more CO and H_2. Decreasing the temperature shifts the equilibrium to the left, producing more C and H_2O.

Tip: A lot of exam questions on this section ask about the effect of increasing temperature, pressure and concentration. But their effect on reaction rate is different to their effect on the position of equilibrium. Make sure you're clear which one you're being asked about.

Adding a catalyst

Catalysts have no effect on the position of equilibrium. They speed up the forward and reverse reactions by the same amount. They can't increase yield — but they do mean equilibrium is reached faster.

Ethanol production

HOW SCIENCE WORKS

The industrial production of ethanol is a good example of why Le Chatelier's principle is important in real life. Ethanol is produced via a reversible exothermic reaction between ethene and steam:

$$C_2H_{4(g)} + H_2O_{(g)} \rightleftharpoons C_2H_5OH_{(g)} \qquad \Delta H = -46 \text{ kJ mol}^{-1}$$

The industrial conditions for the reaction are:

- a pressure of 60-70 atmospheres
- a temperature of 300 °C
- a phosphoric acid catalyst.

Because it's an exothermic reaction, lower temperatures favour the forward reaction. This means that at lower temperatures more ethene and steam is converted to ethanol — you get a better **yield**. But lower temperatures mean a slower rate of reaction. You'd be daft to try to get a really high yield of ethanol if it's going to take you 10 years. So the 300 °C is a compromise between maximum yield and a faster reaction.

Tip: The yield is the amount of product you get from a reaction. Increasing the reaction rate will give you a higher yield in a given time, but you need to shift the equilibrium to increase the maximum yield.

Higher pressures favour the forward reaction, so a pressure of 60-70 atmospheres is used — high pressure moves the reaction to the side with fewer molecules of gas. Increasing the pressure also increases the rate of reaction. Cranking up the pressure as high as you can sounds like a great idea so far. But high pressures are expensive to produce. You need stronger pipes and containers to withstand high pressure. And, in this process, increasing the pressure can also cause side reactions to occur. So the 60-70 atmospheres is a compromise between maximum yield and expense. In the end, it all comes down to minimising costs.

Only a small proportion of the ethene reacts each time the gases pass through the catalyst. To save money and raw materials, the unreacted ethene is separated from the liquid ethanol and recycled back into the reactor. Thanks to this, around 95% of the ethene is eventually converted to ethanol.

Investigating equilibrium position

Some experiments can be used to investigate how equilibrium position changes with changing conditions. The best experiments to highlight these changes are ones where a change in equilibrium position brings about a colour change.

Changing temperature

In a closed system, an increase in temperature will push a reaction at equilibrium in the endothermic direction and a decrease in temperature will push the equilibrium in the exothermic direction.

Example

The brown gas NO_2 exists in equilibrium with the colourless gas N_2O_4. This reversible reaction can be used to investigate the effect of changing temperature on equilibrium position. The forward reaction is exothermic, which means the reverse reaction is endothermic.

Exothermic→

$$\underset{\text{brown}}{2NO_{2(g)}} \rightleftharpoons \underset{\text{colourless}}{N_2O_{4(g)}} \qquad \Delta H = -57.2 \text{ kJ mol}^{-1}$$

←Endothermic

HOW SCIENCE WORKS

To carry out the experiment, place two sealed tubes containing the equilibrium mixture in water baths — one in a warm water bath and one in an ice bath, and observe the colours of the mixtures. The tube in the warm water bath will change to a darker brown colour (Figure 2) as the equilibrium shifts to the left to absorb the extra heat by favouring the endothermic reaction. The tube in the ice bath will go a paler colour (Figure 2) as the equilibrium shifts to the right to replace the lost heat by favouring the exothermic reaction.

Changing concentration

In a closed system, changing the concentrations of either the reactants or products will change the equilibrium position. Adding more reactants will move the equilibrium to the right. Adding more products will move the equilibrium to the left.

Example

Mixing iron(III) nitrate (yellow) and potassium thiocyanate (colourless) solutions results in a reversible reaction where the product is iron(III) thiocyanate (blood red). You end up with the following equilibrium...

$$\underset{\text{yellow}}{Fe^{3+}_{(aq)}} + \underset{\text{colourless}}{SCN^{-}_{(aq)}} \rightleftharpoons \underset{\text{blood red}}{Fe(SCN)^{2+}_{(aq)}}$$

HOW SCIENCE WORKS

The equilibrium mixture is a reddish colour. You can investigate what happens to the equilibrium position when the concentrations of reactants or products are changed by monitoring the colour of the solution.

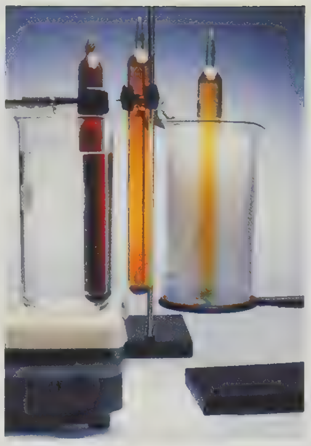


Figure 2: Equilibrium between $NO_{2(g)}$ (brown) and $N_2O_{4(g)}$ (colourless). The tube in the middle is at room temperature. The tube on the left is in a warm water bath. The tube on the right is cooled in ice.

Tip: NO_2 is extremely toxic and can be lethal. If a tube breaks during this experiment, the lab should be evacuated. Remember to carry out a full risk assessment before the experiment.

Tip: It might seem weird that if you add more product you end up with more reactant and vice versa. Make sure you're comfortable with Le Chatelier's principle and it will make more sense.

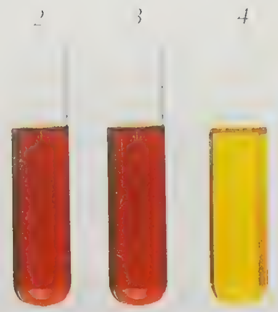


Figure 3: *Test tubes 2, 3 and 4 from the iron(III) thiocyanate equilibrium experiment.*

Add equal amounts of the equilibrium mixture to four test tubes.

- Test tube 1 is the 'control' and nothing is added to it. It keeps its initial reddish colour.
- Add a few drops of iron(III) nitrate solution to test tube 2. The mixture turns a deep red colour (Figure 3).
- Add a few drops of potassium thiocyanate solution to test tube 3. The mixture turns a deep red colour (Figure 3).
- Add a few drops of iron(III) thiocyanate solution to test tube 4. The mixture turns a yellow colour (Figure 3).

When more reactants are added, the equilibrium moves to the right to remove them. The forward reaction is favoured and more product is made (as seen by the deep red colour in test tubes 2 and 3).
When more product is added, the equilibrium moves to the left to remove them. The reverse reaction is favoured and more reactants are made (as seen by the yellowish colour in test tube 4).

Exam Tip
You may get asked why the ideal conditions for a reaction aren't used in reality. Often the answer is to do with the cost of generating the conditions or their safety.

Practice Questions — Application

Q1 An industrial process uses the following reversible reaction:

$$A_{(g)} + 2B_{(g)} \rightleftharpoons C_{(g)} + D_{(g)} \qquad \Delta H = -189\ \text{kJ mol}^{-1}.$$

a) Explain the effect of increasing the concentration of A on the position of the equilibrium.

b) Explain the effect of increasing the pressure on the position of the equilibrium.

c) Explain the effect of increasing the temperature on the position of the equilibrium.

d) Briefly outline the best reaction conditions (in terms of high or low concentration, pressure and temperature) to maximise the production of product D.

Q2 What will be the effect of increasing the pressure on the position of equilibrium of the following reaction?

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$

Explain your answer.

Practice Questions — Fact Recall

Q1 What does it mean if a reaction is in dynamic equilibrium?

Q2 What is Le Chatelier's principle?

Q3 How does the addition of a catalyst affect the position of equilibrium in a reversible reaction?

Q4 Ethanol is produced using a reaction that gives you a higher yield at a low temperature. Explain why a low temperature is not used to produce ethanol industrially.

9. The Equilibrium Constant

Equilibrium constants are important when you're looking at reversible reactions. The next few pages are all about them.

The equilibrium constant, K_c

When you have a homogeneous reaction (where all the reactants and products are in the same physical state) that's reached dynamic equilibrium, you can work out the **equilibrium constant**, K_c, using the concentrations of the products and reactants at equilibrium. K_c gives you an idea of how far to the left or right the equilibrium is. Before you can calculate K_c, you have to write an expression for it. Here's how:

The lower-case letters a, b, d and e are the number of moles of each substance in the equation.

For the general reaction $aA + bB \rightleftharpoons dD + eE$:

$$K_c = \frac{[D]^d[E]^e}{[A]^a[B]^b}$$

The square brackets, [ ], mean concentration in mol dm^{-3}.

The products go on the top line and the reactants go on the bottom line.

Example

For the reaction $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$ there are two reactants (H_2 and I_2) and one product (HI). There's one mole of each of the reactants and two moles of the product so the expression for K_c is:

$$K_c = \frac{[HI]^2}{[H_2]^1[I_2]^1} = \frac{[HI]^2}{[H_2]\,[I_2]}$$

Calculating K_c

If you know the equilibrium concentrations, just bung them in your expression. Then with a bit of help from the old calculator, you can work out the value for K_c. The units are a bit trickier though — they vary, so they're not the same for every reaction.

Example **Maths Skills**

For the hydrogen iodide example above, the equilibrium concentrations are: [HI] = 0.80 mol dm^{-3}, $[H_2]$ = 0.10 mol dm^{-3} and $[I_2]$ = 0.10 mol dm^{-3} at 640 K. What is the equilibrium constant for this reaction at 640 K?

Just stick the concentrations into the expression for K_c:

$$K_c = \frac{[HI]^2}{[H_2]\,[I_2]} = \frac{0.8^2}{0.1 \times 0.1} = 64$$

To work out the units of K_c put the units in the expression instead of the numbers:

$$K_c = \frac{(\text{mol dm}^{-3})^2}{(\text{mol dm}^{-3})(\text{mol dm}^{-3})} = \frac{\cancel{(\text{mol dm}^{-3})}\cancel{(\text{mol dm}^{-3})}}{\cancel{(\text{mol dm}^{-3})}\cancel{(\text{mol dm}^{-3})}}$$

The concentration units cancel, so there are no units and K_c is just **64**.

Learning Objectives:

- Deduce expressions for the equilibrium constant, K_c, for homogeneous reactions.
- Calculate the values of the equilibrium constant, K_c, from provided equilibrium concentrations.
- Estimate the position of equilibrium from the magnitude of K_c.

Specification Reference 3.2.3

Exam Tip

In exam questions on K_c you'll often be told the temperature. You don't need this value for your calculation — it's just so you know the temperature is constant.

Tip: Don't forget — when you're calculating K_c the products go on the top line and the reactants go on the bottom line.

Exam Tip

K_c has no units in this example but this won't always be the case. You will need to know how to work out the units for the A level exams.

Tip: If the units end up as (1 / mol dm^{-3}), you write that as mol^{-1} dm^3.

Tip: If K_c is large, at equilibrium there will be lots of product and not much reactant. If K_c is small, it's the other way around — at equilibrium there'll be loads of reactant but not much product.

A change in temperature can change the position of equilibrium so K_c varies with temperature. That's why you'll often be asked what K_c is at a specific temperature.

Estimating the position of equilibrium

K_c will increase when the quantities of the products increase and the quantities of the reactants decrease. So an increase in K_c means the equilibrium has shifted to the right. If K_c decreases, that means the quantities of reactants have increased and the quantities of products have decreased, so the equilibrium has moved to the left. The greater the increase or decrease in K_c is, the more the equilibrium has moved.

Practice Questions — Application

Q1 The following equilibrium exists under certain conditions:

$$C_2H_4 + H_2O \rightleftharpoons C_2H_5OH$$

Write out the expression for the equilibrium constant, K_c, for this reaction.

Q2 Under certain conditions the following equilibrium is established:

$$2SO_2 + O_2 \rightleftharpoons 2SO_3$$

a) Write out an expression for K_c for this reaction.

At a certain temperature the equilibrium concentrations for the three reagents were found to be:

$SO_2 = 0.250 \text{ mol dm}^{-3}$, $O_2 = 0.180 \text{ mol dm}^{-3}$, $SO_3 = 0.360 \text{ mol dm}^{-3}$

b) Calculate K_c for this equilibrium.

Practice Questions — Fact Recall

Q1 Write out an expression for K_c for the general reaction:

$$aA + bB \rightleftharpoons dD + eE$$

Q2 Why is K_c often given at a certain, stated temperature?

Q3 K_c for a certain reaction at equilibrium is 0.012 at 298 K. For the same reaction at 350 K, the value of K_c was found to be 2.048. What is the effect of increasing the temperature on the position of equilibrium for this reaction?

Section Summary

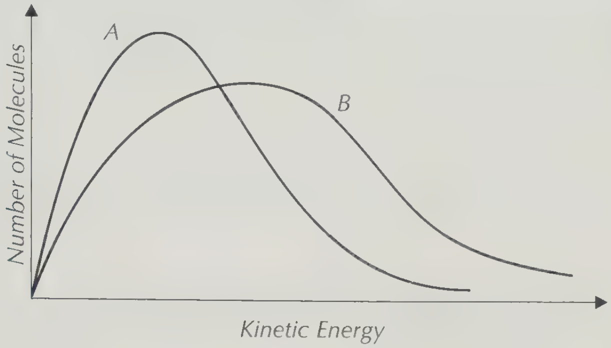
Make sure you know...

- That 'standard conditions' mean 100 kPa and 298 K and 'standard state' means the physical state of a substance under standard conditions.
- That enthalpy change, ΔH (in kJ mol^{-1}), is the heat energy transferred in a reaction at constant pressure.
- That ΔH° is the enthalpy change for a reaction where the reactants and products are in their standard states and the measurements are made at 100 kPa pressure and a stated temperature (usually 298 K).
- That $\Delta_r H^{\circ}$ is the enthalpy change when a reaction occurs in the molar quantities shown in the chemical equation, under standard conditions with all reactants and products in their standard states.
- That $\Delta_f H^{\circ}$ is the enthalpy change when 1 mole of a compound is formed from its elements in their standard states under standard conditions.
- That $\Delta_c H^{\circ}$ is the enthalpy change when 1 mole of a substance is completely burned in oxygen under standard conditions.
- That $\Delta_{neut} H^{\circ}$ is the enthalpy change when solutions of an acid and an alkali react together to form 1 mole of water, under standard conditions.
- That exothermic reactions give out energy, so ΔH is negative.
- That endothermic reactions absorb energy, so ΔH is positive.
- How to draw and interpret an enthalpy profile diagram for a reaction, identifying the activation energy, the enthalpy change of the reaction, and whether the reaction is exothermic or endothermic.
- That the minimum amount of kinetic energy required for a reaction is called the activation energy.
- That average bond enthalpies tell us the energy needed to break one mole of bonds in the gas phase, averaged over many different compounds.
- How to use average bond enthalpies to calculate enthalpy changes for reactions, using the equation: Enthalpy change of reaction = Total energy absorbed – Total energy released.
- How to measure enthalpy changes directly in the lab.
- How to calculate the heat lost or gained (q) by a reaction in the laboratory using the equation $q = mc\Delta T$, where m is the mass of the reaction mixture, c is its specific heat capacity, and ΔT is the temperature change due to the reaction.
- That Hess's Law says that:
  The total enthalpy change of a reaction is always the same, no matter which route is taken.
- How to use Hess's Law to calculate enthalpy changes for reactions from other enthalpies of reaction.
- How to use Hess's Law to calculate enthalpy changes for reactions from enthalpies of formation.
- How to use Hess's Law to calculate enthalpy changes for reactions from enthalpies of combustion.
- That the Boltzmann distribution describes the spread of energies of the molecules in a liquid or gas.
- How to draw and interpret Boltzmann distribution curves for substances at different temperatures.
- That increasing the concentration of reactants (or the pressure if they're gases) will increase the reaction rate, because the molecules will be closer together and so more likely to collide and react.
- That a catalyst is a substance that increases the rate of a reaction by providing an alternative pathway with a lower activation energy, and is chemically unchanged at the end of the reaction.
- That catalysts do not change the shape of Boltzmann distribution curves.
- That heterogeneous catalysts are in a different physical state to the reactants and homogeneous catalysts are in the same physical state as the reactants.
- That catalysts have a great economic importance.
- That using catalysts has benefits in terms of environmental sustainability.
- How to measure the rates of chemical reactions, including the measurement of mass and gas volume.

- How to calculate the rate of a reaction using the gradient of a graph showing how a physical quantity changes over time.
- That reversible reactions can reach an equilibrium, where the concentrations of reactants and products stay constant and the forwards and backwards reactions have the same reaction rate.
- That Le Chatelier's principle states that "if there's a change in concentration, pressure or temperature, the equilibrium will move to help counteract the change."
- That increasing the concentration of a reactant shifts the equilibrium to remove the extra reactant.
- That increasing the pressure shifts the equilibrium in favour of the reaction that produces the fewest moles of gas, in order to reduce the pressure.
- That increasing the temperature shifts the equilibrium in favour of the endothermic reaction, to remove the excess heat. (Low temperatures favour exothermic reactions.)
- That a catalyst does not affect the position of equilibrium in a reversible reaction.
- Why there sometimes has to be a compromise between chemical equilibrium and reaction rate in industry.
- How to describe the experimental techniques used to investigate how changes in concentration and temperature affect the position of equilibrium.
- That K_c is the equilibrium constant.
- How to deduce expressions for the equilibrium constant, K_c.
- How to calculate K_c and its units from the equilibrium concentrations for a reaction.
- How to estimate the position of equilibrium from the magnitude of K_c.

Exam-style Questions

1 Two Boltzmann energy distributions for molecules of a gas are shown below.



(a) What does the kinetic energy value at the maximum height on curve A represent?

A The total number of molecules in the distribution.

B The most likely energy of molecules in the distribution.

C The activation energy of the reaction.

D The enthalpy change of formation for the molecule.

(1 mark)

(b) What does distribution B represent?

A Distribution A at lower concentration.

B Distribution A at lower temperature.

C Distribution A at higher temperature.

D Distribution A at higher concentration.

(1 mark)

2 1.5 g of magnesium is added to a conical flask containing 40 cm^3 1.0 mol dm^{-3} hydrochloric acid and the volume of hydrogen gas given off is measured, over time, using a gas syringe. A series of identical experiments is then carried out with increasing concentrations of hydrochloric acid to see what effect this has on the rate of reaction. Which of the following variables is the independent variable in the experiment?

A Concentration of hydrochloric acid.

B Volume of hydrochloric acid.

C Mass of magnesium added.

D Volume of hydrogen gas produced.

(1 mark)

3 A chemical factory produces ethanol (C_2H_5OH) from ethene (C_2H_4) and steam, using the following reversible reaction:

$C_2H_{4(g)} + H_2O_{(g)} \rightleftharpoons C_2H_5OH_{(g)}$ $\Delta H = -46\ \text{kJ mol}^{-1}$

The reaction is carried out under the following conditions:

Pressure = 60 atm
Temperature = 300 °C
Catalyst = phosphoric acid

(a) Without the phosphoric acid catalyst the rate of reaction is so slow that dynamic equilibrium takes a very long time to be reached.

Describe what it means for a reaction to be at dynamic equilibrium.

(2 marks)

(b) The conditions for the reaction were chosen with consideration to Le Chatelier's principle. Explain why the pressure chosen for the process is a compromise.

(3 marks)

(c) A leak in one of the pipes reduces the amount of steam in the reaction mixture.

Explain the effect this has on the maximum yield of ethanol.

(3 marks)

(d) The equilibrium concentrations are: $[C_2H_5OH] = 2.70\ \text{mol dm}^{-3}$, $[C_2H_4] = 0.400\ \text{mol dm}^{-3}$ and $[H_2O] = 0.400\ \text{mol dm}^{-3}$.

Calculate the equilibrium constant for this reaction at 60 atm and 300 °C.

(2 marks)

4 Two gases react together in an exothermic reaction.

The reaction has an activation energy of $90\ \text{kJ mol}^{-1}$.

The enthalpy change for the reaction is $-150\ \text{kJ mol}^{-1}$.

(a) (i) In terms of collision theory, what is meant by the term 'activation energy'?

(2 marks)

(ii) Sketch the enthalpy profile diagram for the reaction.

Label your diagram to show the axis labels, the activation energy and the enthalpy change of the reaction.

(4 marks)

(b) The reactants are heated.

Explain the effect this will have on the rate of the reaction.

(3 marks)

(c) Explain the effect that lowering the pressure has on the rate of the reaction.

(3 marks)

(d) A catalyst is added to the reaction.

(i) Define the term catalyst.

(1 mark)

(ii) Explain how a catalyst increases the rate of reaction using an enthalpy profile diagram and a Boltzmann distribution curve.

You should organise your answer and use the correct technical terms.

(6 marks)

5 The table below shows the standard enthalpy change of combustion, $\Delta_c H^\circ$, for carbon, hydrogen and octane ($C_8H_{18(l)}$).

The standard enthalpy of formation of octane can be calculated from this data using Hess's Law.

	$\Delta_c H^\circ$
$C_{(s)}$	–394 kJ mol^{-1}
$H_{2(g)}$	–286 kJ mol^{-1}
$C_8H_{18(l)}$	–5470 kJ mol^{-1}

(a) Write a balanced chemical equation for the complete combustion of octane.

(1 mark)

(b) (i) Use your answer to part **(a)** and the data in the table above to calculate the standard enthalpy change of formation of octane, $\Delta_f H^\circ$.

(3 marks)

(ii) State whether the formation of octane is exothermic or endothermic.

Explain your answer.

(2 marks)

(c) A calorimeter, containing 325 g of water (c = 4.18 J g^{-1} K^{-1}), was used to measure the enthalpy change of combustion of octane (M_r = 114). 0.4503 g of octane was burnt, which increased the temperature of the water by 13.0 K.

(i) Calculate the measured enthalpy change of combustion of octane.

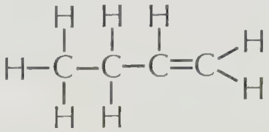
(2 marks)

(ii) Give two possible reasons why the measured enthalpy change of combustion is different to the value given in the table above.

(2 marks)

6 Alkenes are very important in the chemical industry.

(a) The structure of the alkene but-1-ene is shown below.



But-1-ene will burn completely in oxygen to produce CO_2 and H_2O.

The table below shows bond enthalpies for the bonds present in the reactants and products of this combustion reaction.

Bond	Bond Enthalpy (Average value except where stated)
C–H	+413 kJ mol^{-1}
C=C	+612 kJ mol^{-1}
C–C	+347 kJ mol^{-1}
O=O	+498 kJ mol^{-1}
C=O (in CO_2)	+805 kJ mol^{-1}
O–H (in H_2O)	+460 kJ mol^{-1}

These bond enthalpies can be used to calculate the standard enthalpy change of combustion for but-1-ene.

(i) State the meaning of the term 'standard enthalpy change of combustion', $\Delta_c H^{\circ}$.

(3 marks)

(ii) Use the data in the table to calculate a value for the standard enthalpy change of combustion for but-1-ene.

(3 marks)

(iii) The standard enthalpy change of combustion for but-1-ene calculated from the average bond enthalpies is different to the value given in the data book. Suggest why.

(1 mark)

(b) 0.0215 mol of another alkene are burned. The energy released heats 200 cm^3 water from 21.0 °C to 53.8 °C.

(density of water = 1.00 g cm^{-3}, specific heat capacity of water = 4.18 J g^{-1} K^{-1})

(i) Calculate the amount of energy released in kJ when the alkene is burned.

(2 marks)

(ii) Calculate the enthalpy change of combustion, $\Delta_c H^{\circ}$, of the alkene.

(2 marks)

(iii) Explain, in terms of making and breaking bonds, why the combustion of the alkene is exothermic.

(2 marks)

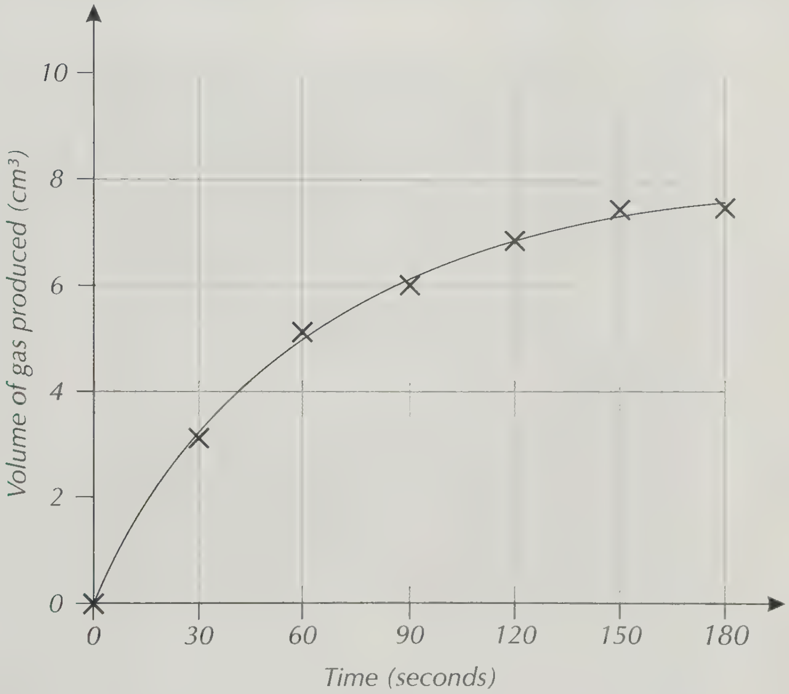
7 When calcium is reacted with water, calcium hydroxide and hydrogen gas are produced, according to the equation below.

$$Ca_{(s)} + H_2O_{(l)} \rightarrow CaO_{(s)} + H_{2(g)}$$

(a) Describe a method which could be used to measure the volume of hydrogen gas released over time.

(2 marks)

(b) The reaction was carried out and the volume of hydrogen produced was measured at 30 second intervals. A graph showing the results is given below.



Calculate the rate of reaction at 1 minute.

(3 marks)

Learning Objective:

- Know that a functional group is a group of atoms responsible for the characteristic reactions of a compound.

Specification Reference 4.1.1

1. Organic Chemistry

Organic chemistry is the study of carbon-containing compounds. Here's a brief introduction to some of the basic concepts you'll need to get your head around before you can study organic chemistry in more detail.

The basics

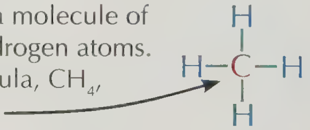
There are a few basic concepts in organic chemistry which you need to understand to really get on with this module.

Nomenclature

There are thousands, if not millions, of known organic compounds and it would be pretty silly if we didn't have an easy way to describe them. That's where **nomenclature** comes in. Don't be put off by the long name, all it means is naming molecules using specific rules. These rules (known as the IUPAC system for naming organic compounds) allow scientists to discuss organic chemistry safe in the knowledge that they're all talking about the same molecules. It means that some molecules end up with really long and complicated looking names (e.g. 1,2-dichloro-3-methylbutane) but once you know the rules, it's easy to work out what they all mean. There's more about nomenclature on pages 211-213.

Formulas

Picturing molecules can be pretty difficult when you can't see them all around you. We can use the elemental symbols from the periodic table to help visualise molecules. For example, a molecule of methane is one carbon atom attached to four hydrogen atoms. You could show this by giving its molecular formula, CH_4, or you could draw its displayed formula like this:



$$\begin{array}{c} H \\ | \\ H-C-H \\ | \\ H \end{array}$$

There's more on formulas on pages 203-205. This isn't exactly what methane looks like, but visualising it like this lets us compare it to other molecules and means we can predict its properties and how it might react with other molecules. Molecular models can also be used to represent molecules (see Figure 1).

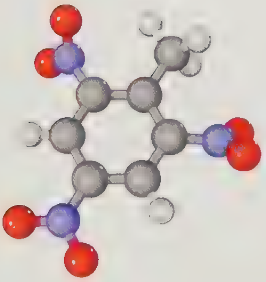
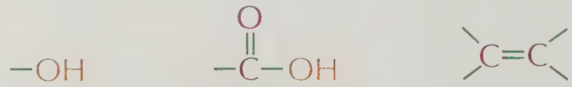


Figure 1: *A molecular model of a TNT molecule. Each grey sphere represents a carbon atom, each white sphere represents a hydrogen atom, the purple ones represent nitrogen atoms and the red ones oxygen atoms.*

Functional groups

The functional group of a molecule is the group of atoms that's responsible for its characteristic reactions — it's where all the interesting stuff happens. They're usually pretty easy to spot because they're the bits which aren't just hydrogen and carbon atoms (e.g. bromine atoms, oxygen atoms, etc.). You'll come across a few different functional groups in this Module — here are a few examples...



Functional groups of... alcohols carboxylic acids alkenes

For now, remember that carbon atoms have four bonds, hydrogen atoms have one bond and oxygen atoms have two bonds joining them to other atoms.

So there you go. That's pretty much all you need to know to get started.

Tip: That stuff about carbon atoms making four bonds, hydrogen making one bond and oxygen making two is right most of the time, but isn't always the case. The good news is that you don't need to worry about that right now.

2. Formulas

Organic compounds can be represented in lots of different ways, using different types of formulas. You need to be familiar with what these formulas show and how to switch between them.

Types of formulas

General formulas and homologous series

A **general formula** is an algebraic formula that can describe any member of a family of compounds. For example, alcohols have the general formula $C_nH_{2n+1}OH$. Organic chemistry is more about groups of similar chemicals than individual compounds. These groups are called **homologous series**. A homologous series is a family of compounds that have the same functional group and general formula. Consecutive members of a homologous series differ by $-CH_2-$.

Example

The simplest homologous series is the alkanes. They're straight chain molecules that contain only carbon and hydrogen atoms. There are always twice as many hydrogen atoms as carbon atoms, plus two more. So the general formula for alkanes is C_nH_{2n+2}. You can use this formula to work out how many hydrogen atoms there are in any alkane if you know the number of carbon atoms. For example...

- If an alkane has 1 carbon atom, n = 1.
  This means the alkane will have (2 × 1) + 2 = 4 hydrogen atoms.
  So the molecular formula of this alkane would be CH_4 (you don't need to write the 1 in C_1).
- If an alkane has 5 carbon atoms, n = 5.
  This means the alkane will have (2 × 5) + 2 = 12 hydrogen atoms.
  So its molecular formula would be C_5H_{12}.
- If an alkane has 15 carbon atoms, n = 15.
  This means the alkane will have (2 × 15) + 2 = 32 hydrogen atoms.
  So its molecular formula is $C_{15}H_{32}$.

Molecular formulas

A molecular formula gives the actual number of atoms of each element in a molecule.

Examples

Ethane has the molecular formula C_2H_6 — each molecule is made up of 2 carbon atoms and 6 hydrogen atoms.

- Pentene has the molecular formula C_5H_{10} — each molecule is made up of 5 carbon atoms and 10 hydrogen atoms.
- 1,4-dibromobutane has the molecular formula $C_4H_8Br_2$ — each molecule is made up of 4 carbon atoms, 8 hydrogen atoms and 2 bromine atoms.
- 1,3-dichloropropane has the molecular formula $C_3H_6Cl_2$ — each molecule is made up of 3 carbon atoms, 6 hydrogen atoms and 2 chlorine atoms.

Learning Objectives:

- Know that a general formula is the simplest algebraic formula of a member of a homologous series.
- Be able to define a homologous series as a series of organic compounds with the same functional group but where each successive member differs by CH_2.
- Be able to use the general formula of a homologous series to predict the formula of any member of the series.
- Know that a structural formula gives the minimal detail that shows the arrangement of atoms in a molecule.
- Know that a displayed formula shows the relative positioning of atoms and the bonds between them.
- Know that a skeletal formula is a simplified organic formula, shown by removing hydrogen atoms from alkyl chains, leaving just a carbon skeleton and associated functional groups.

Specification Reference 4.1.1

Tip: Molecular formulas tell you what atoms are in a molecule, but they don't tell you which atoms are bonded to which.

Tip: Like organic compounds, inorganic compounds have empirical and molecular formulas too. There's more about these formulas on page 60.

Empirical formulas

An empirical formula gives the simplest whole number ratio of atoms of each element in a compound. To find the empirical formula you have to divide the molecular formula by the smallest number of atoms for a given element in the molecule. For example, if the molecular formula is $C_2H_4Cl_2$, the smallest number of atoms is 2 (for both C and Cl). So you divide the molecular formula by 2 and get the empirical formula CH_2Cl. The number of each type of atom in the empirical formula needs to be a whole number. So if you divide the molecular formula by the smallest number of atoms and end up without whole numbers, the molecular formula will be the same as the empirical formula.

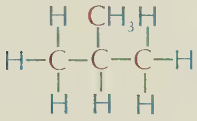
Exam Tip
You don't have to learn the definitions for the different formulas off by heart, but you do have to know what they are and be able to use them.

Examples

Name	Molecular Formula	Divide by...	Empirical Formula
Ethane	C_2H_6	2	CH_3
Pentene	C_5H_{10}	5	CH_2
1,4-dichlorobutane	$C_4H_8Cl_2$	2	C_2H_4Cl
1,3-dichloropropane	$C_3H_6Cl_2$	-	$C_3H_6Cl_2$
1,2,3-trichloroheptane	$C_7H_{13}Cl_3$	-	$C_7H_{13}Cl_3$

In the last two examples in the table, the molecular formula is the same as the empirical formula — you can't divide by the smallest number of atoms for a given element and still get whole numbers.

Tip: It's easy to see how most groups are written in a structural formula, but there are a few things to watch out for. Carboxylic acid groups are written as COOH, and ester groups as COO. Any branches that are more than one atom long on the carbon chain are put in brackets, e.g. methylpropane...



... has the structural formula $CH_3CH(CH_3)CH_3$.

Structural formulas

A structural formula shows the atoms carbon by carbon, with the attached hydrogens and functional groups.

Examples

Ethane has the structural formula CH_3CH_3.

Pentene has the structural formula $CH_3CH_2CH_2CHCH_2$.

1,4-dibromobutane has the structural formula $BrCH_2CH_2CH_2CH_2Br$.

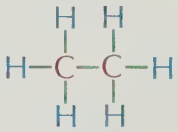
1,3-dichloropropane has the structural formula $ClCH_2CH_2CH_2Cl$.

Displayed formulas

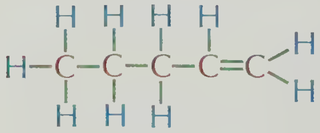
A displayed formula shows how all the atoms are arranged, and all the bonds between them.

Examples **Maths Skills**

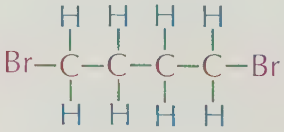
Displayed formula of ethane:



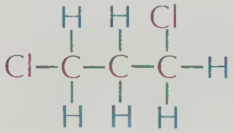
Displayed formula of pentene:



Displayed formula of 1,4-dibromobutane:



Displayed formula of 1,3-dichloropropane:



Tip: The great thing about all these formulas is that they're used all over the world. So they give scientists a way of communicating information about organic compounds without any room for misinterpretation.

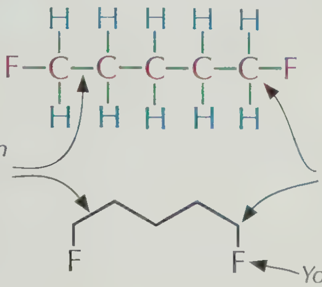
HOW SCIENCE WORKS

Skeletal formulas

A skeletal formula shows the bonds of the carbon skeleton only, with any functional groups. The hydrogen and carbon atoms that are part of the main carbon chain aren't shown. This is handy for drawing large complicated structures, like cyclic hydrocarbons. The carbon atoms are found at each junction between bonds and at the end of bonds (unless there's already a functional group there). Each carbon atom has enough hydrogen atoms attached to make the total number of bonds from the carbon up to four.

Examples — Maths Skills

Displayed and skeletal formulas of 1,5-difluoropentane:

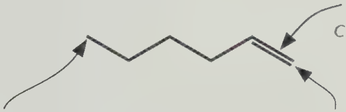


The carbon-carbon bonds stay where they are.

Each junction represents one carbon atom.

You still have to show the atoms that aren't carbon or hydrogen.

Skeletal formula of hex-1-ene:



A double line represents a carbon-carbon double bond.

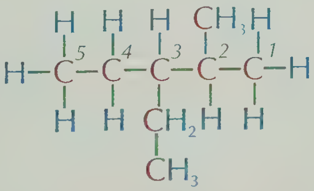
This carbon atom only has one carbon-carbon bond drawn on the molecule. This means that it has three hydrogen atoms attached to make the number of bonds up to four.

This carbon atom has a carbon-carbon double bond, so it must have two hydrogen atoms attached to make the number of bonds up to four.

Practice Questions — Application

Q1 2-bromopropane has the structural formula $CH_3CHBrCH_3$. Draw the displayed formula of 2-bromopropane.

Q2 Here is the structure of 3-ethyl-2-methylpentane.



Write down the molecular formula for 3-ethyl-2-methylpentane.

Q3 Write down the empirical formula of the following compounds:

a) C_2H_4

b) $C_8H_{14}Br_2$

c) $C_9H_{17}Cl_3$

Exam Tip
Skeletal formulas are notoriously difficult to draw in an exam without making any mistakes... If you're not 100% happy with them stick to displayed formulas — you don't want to introduce silly errors into your answers. Of course, if the exam question asks for a skeletal formula you've got no choice — just give it your best shot.

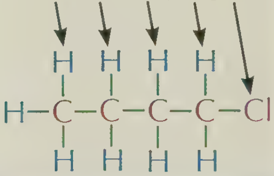
Tip: You have to draw skeletal formulas as zig-zag lines, otherwise you can't tell where one bond ends and the next begins.

HOW SCIENCE WORKS

Tip: The various types of formula have different levels of detail, so which one you use depends on what you're trying to show. The trick is to know which formula will give all the information you're trying to show, without being over-complicated.

Tip: Drawing a displayed formula from a structural formula is dead easy — just draw it out exactly as it's written:

$CH_3CH_2CH_2CH_2Cl$



Exam Tip
It's really important to double-check your answers for questions like these. It's so easy to miscount the number of different atoms, but getting it right means easy marks in the exam.

Q4 Alkenes have the general formula C_nH_{2n}.

a) Butene is an alkene with 4 carbon atoms. Write the molecular formula of butene.

b) Heptene is an alkene with 7 carbon atoms. How many hydrogen atoms does it contain?

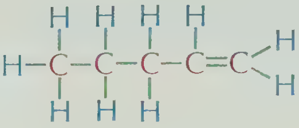
Q5 1,2-dibromopropane has the structural formula $CH_3CHBrCH_2Br$.

a) Write down the molecular formula of 1,2-dibromopropane.

b) Draw the displayed formula of 1,2-dibromopropane.

c) Write the empirical formula of 1,2-dibromopropane.

Q6 Here is the displayed formula of pent-1-ene.



a) Write down the molecular formula of pent-1-ene.

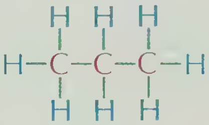
b) Write down the structural formula of pent-1-ene.

c) What is the empirical formula of pent-1-ene?

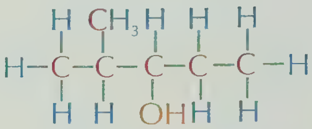
Tip: At the moment, it doesn't matter whether you show atoms bonding above, below or to the side of a carbon atom, they all mean the same thing — it's which atoms they're bonding to that's the important thing.

Q7 Draw skeletal formulas of the molecules below:

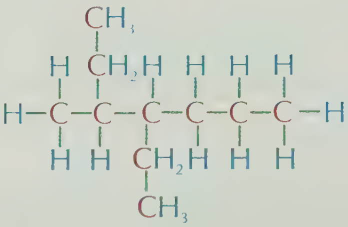
a)



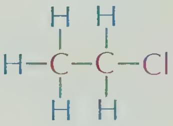
b)



c)

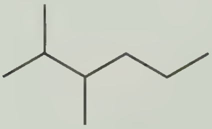


d)

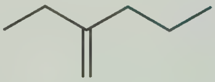


Q8 Give structural formulas for the molecules below:

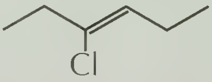
a)



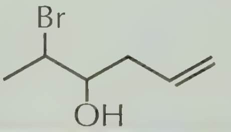
b)



c)



d)



Exam Tip
You need to make sure you know which type of formula is which. You won't get any marks for writing a structural formula if the examiner wants a molecular one.

Practice Questions — Fact Recall

Q1 What is the formula used to represent a homologous series called?

Q2 What is a homologous series?

Q3 What does a displayed formula show?

Q4 The symbols of which atoms aren't shown in a skeletal formula?

3. Carbon Skeletons

All organic compounds have a carbon skeleton. This is just the arrangement of all the carbon atoms in the molecule, ignoring any functional groups. Carbon skeletons can be split into two groups — aromatic and aliphatic.

Aromatic compounds

Aromatic compounds contain a benzene ring. All you need to know about benzene for now is how you recognise or draw it (see Figure 1).

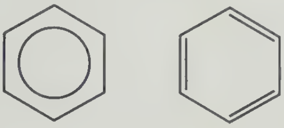
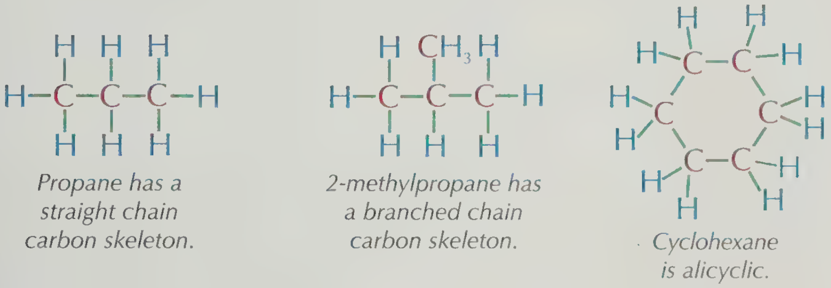


Figure 1: *Two representations of a benzene ring.*

Aliphatic compounds

Aliphatic compounds contain carbon and hydrogen joined together in straight chains, branched chains or non-aromatic rings (see Figure 2). If an aliphatic compound contains a (non-aromatic) ring, then it can be called **alicyclic**.



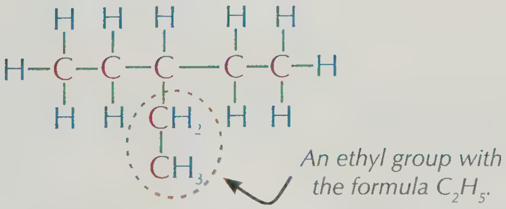
Propane has a straight chain carbon skeleton.

2-methylpropane has a branched chain carbon skeleton.

Cyclohexane is alicyclic.

Figure 2: *Different types of aliphatic compound.*

In compounds with a branched carbon skeleton, any hydrocarbon branched chains are called **alkyl groups**. Alkyl groups have the general formula C_nH_{2n+1}.



An ethyl group with the formula C_2H_5.

Figure 3: *The ethyl group in a molecule of 3-ethylpentane.*

Organic compounds can have **saturated** or **unsaturated** carbon skeletons. Saturated compounds only contain carbon-carbon single bonds — like alkanes. Unsaturated compounds can have carbon-carbon double bonds, triple bonds or aromatic groups.

Practice Questions — Application

Q1 A propyl group is an alkyl group containing three carbon atoms. What is the molecular formula of a propyl group?

Q2 The organic compound butene contains a C=C double bond. Is it saturated or unsaturated?

Learning Objectives:

- Know that an aromatic compound contains a benzene ring.
- Know that aliphatic compounds contain carbon and hydrogen joined together in straight chains, branched chains or non-aromatic rings.
- Know that alicyclic compounds are aliphatic compounds arranged in non-aromatic rings with or without side chains.
- Know that alkyl groups have the general formula C_nH_{2n+1}.
- Know that saturated compounds have single carbon-carbon bonds only and unsaturated compounds contain multiple carbon-carbon bonds, including C=C, C≡C and aromatic rings).

Specification Reference 4.1.1

Tip: The representations of benzene in Figure 1 show its skeletal formula (see page 205). Each point represents a carbon atom, and the lines are the bonds between them. There is also a hydrogen bonded to each carbon, but these aren't shown in skeletal formulas.

Learning Objectives:

- Know that structural isomers are compounds with the same molecular formula but different structural formulas.
- Be able to determine the possible structural formulas of an organic molecule, given its molecular formula.

Specification Reference 4.1.1

4. Structural Isomers

You can put the same atoms together in different ways to make completely different molecules. Two molecules are isomers if they have the same molecular formula but the atoms are arranged differently.

What are structural isomers?

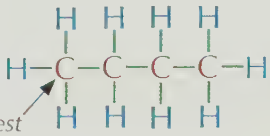
In structural isomers, the molecular formula is the same, but the structural formula is different. There are three different types of structural isomer.

1. Chain isomers

The carbon skeleton can be arranged differently — for example, as a straight chain, or branched in different ways. Molecules that have different arrangements of the carbon skeleton are called **chain isomers**.

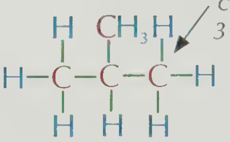
Examples — Maths Skills

There are different chain isomers of C_4H_{10}. The diagrams below show the straight chain isomer butane and a branched chain isomer methylpropane.



Here the longest carbon chain is 4 carbon atoms.

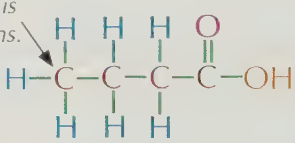
butane



Here the longest carbon chain is 3 carbon atoms.

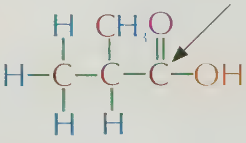
methylpropane

There are different chain isomers of $C_4H_8O_2$. The diagrams below show the straight chain isomer butanoic acid and a branched chain isomer methylpropanoic acid.



Here the longest carbon chain is 4 carbon atoms.

butanoic acid



Here the longest carbon chain is 3 carbon atoms.

methylpropanoic acid

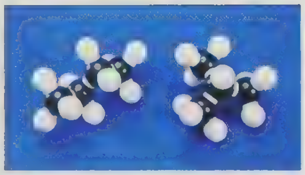


***Figure 1:** Molecular models showing two chain isomers of C_4H_{10} — butane (left) and methylpropane (right).*

Chain isomers have similar chemical properties — but their physical properties, like boiling point, will be different because of the change in shape of the molecule.

Exam Tip

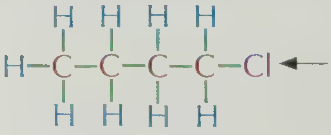
You don't always have to draw all of the bonds when you're drawing a molecule — writing CH_3 next to a bond is just as good as drawing out the carbon atom, three bonds and three hydrogen atoms. But if you're asked for a displayed formula you must draw out all of the bonds to get the marks.

2. Positional isomers

The skeleton and the functional group could be the same, only with the functional group attached to a different carbon atom. These are called **positional isomers**.

Example — Maths Skills

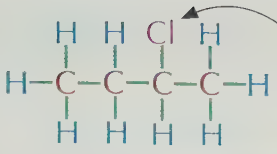
There are two positional isomers of C_4H_9Cl. The chlorine atom is attached to different carbon atoms in each isomer.



The Cl is attached to the first carbon atom.

1-chlorobutane

Tip: If the chlorine atom was attached to the carbon atom on the left, it would still be the same molecule — just drawn the other way round. It would still be 1-chlorobutane.



2-chlorobutane

The Cl is attached to the second carbon atom.

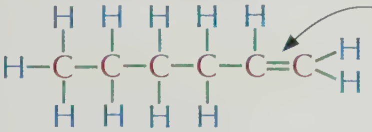
Positional isomers also have different physical properties, and the chemical properties might be different too.

3. Functional group isomers

Functional group isomers have the same atoms arranged into different functional groups.

Example — **Maths Skills**

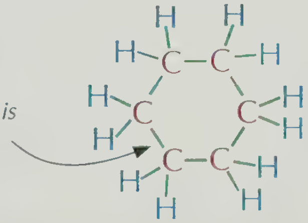
The formulas below show two functional group isomers of C_6H_{12}.



hex-1-ene

The functional group is the C=C — it's an alkene.

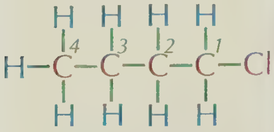
This molecule is an alkane.

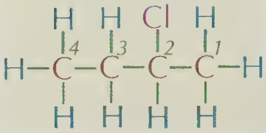


cyclohexane

Functional group isomers have very different physical and chemical properties.

Tip: Number the carbon atoms — it makes it easier to see what the longest carbon chain is and where side chains and atoms are attached:





Identifying isomers

Atoms can rotate as much as they like around single C–C bonds. Remember this when you work out structural isomers — sometimes what looks like an isomer, isn't.

Exam Tip

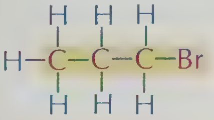
To avoid mistakes when you're identifying isomers in an exam, draw the molecule so the longest carbon chain goes left to right across the page. This will make it easier to see the isomers.

Examples — **Maths Skills**

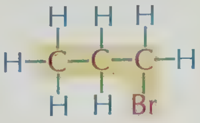
There are only two positional isomers of C_3H_7Br:

1-bromopropane

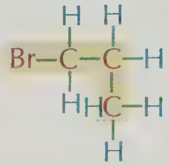
The Br is always on the first carbon atom.



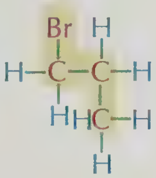
1-bromopropane



1-bromopropane again...



...and again...

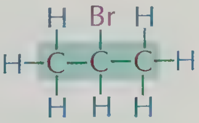


and again.

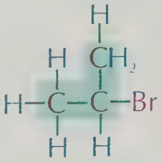
All these molecules are the same, they're just drawn differently.

2-bromopropane

The Br is always on the second carbon atom.

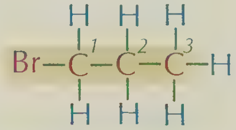


2-bromopropane



2-bromopropane again

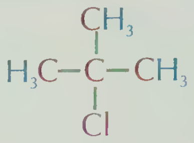
Tip: In propane, the Br can only really go on the first or second carbon atom. If it was on the "third" it would be the same as being on the first again because you start counting from whichever end the Br is on.



1-bromopropane

Practice Questions — Application

Q1 Here is an isomer of chloro-2-methylpropane.

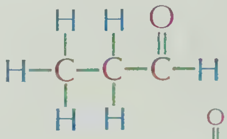


$$\begin{array}{ccccc} & & CH_3 & & \\ & & | & & \\ H_3C & - & C & - & CH_3 \\ & & | & & \\ & & Cl & & \end{array}$$

Draw the other positional isomer of chloro-2-methylpropane.

Q2 Draw all the chain isomers of C_5H_{12}.

Q3 Here is the displayed formula of propanal.

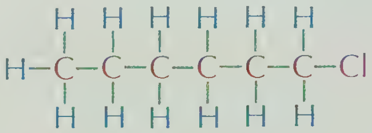


$$\begin{array}{ccccccccc} & & H & & H & & O & & \\ & & | & & | & & \| & & \\ H & - & C & - & C & - & C & - & H \\ & & | & & | & & & & \\ & & H & & H & & & & \end{array}$$

Propanal has the functional group $\overset{O}{\overset{\|}{C}}-H$.

Draw an isomer of propanal with the functional group $\overset{O}{\overset{\|}{C}}$.

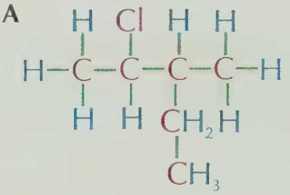
Q4 Here is the displayed formula of 1-chlorohexane.



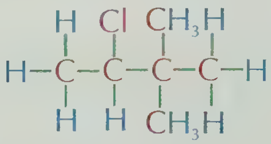
$$\begin{array}{ccccccccccccccc} & & H & & H & & H & & H & & H & & H & & \\ & & | & & | & & | & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & C & - & C & - & C & - & Cl \\ & & | & & | & & | & & | & & | & & | & & \\ & & H & & H & & H & & H & & H & & H & & \end{array}$$

a) Which of the molecules (**A–D**) are isomers of 1-chlorohexane?

A

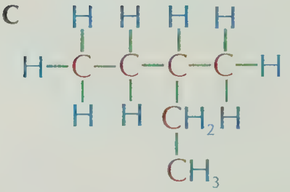


B

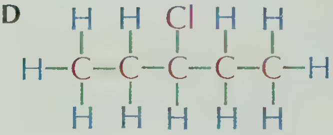


$$\begin{array}{ccccccccccc} & & H & & Cl & & CH_3 & & H & & \\ & & | & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & | & & \\ & & H & & H & & CH_3 & & H & & \end{array}$$

C



D



$$\begin{array}{ccccccccccccc} & & H & & H & & Cl & & H & & H & & \\ & & | & & | & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & | & & | & & \\ & & H & & H & & H & & H & & H & & \end{array}$$

b) State the type of isomerism shown in part a).

Exam Tip
Be really careful when you're drawing out functional group isomers that you do draw a different isomer and not just the same isomer again in a slightly different way — numbering the carbons and making sure the functional group's on a different one might help.

Exam Tip
If you get confused between different isomers of a molecule, try drawing the structure of the molecule out again in a slightly different way — everything might become clear.

Practice Questions — Fact Recall

Q1 What are isomers?

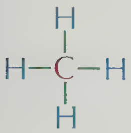
Q2 What are structural isomers?

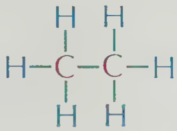
5. Alkanes and Nomenclature

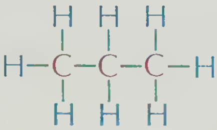
Alkanes are molecules with hydrogen atoms, carbon atoms and single bonds. Nomenclature is just a fancy word for naming organic compounds.

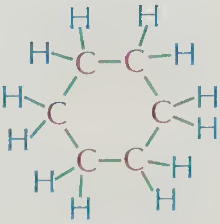
Structure of alkanes

Alkanes have the general formula C_nH_{2n+2}. They've only got carbon and hydrogen atoms, so they're **hydrocarbons**. Every carbon atom in an alkane has four single bonds with other atoms. It's impossible for carbon to make more than four bonds, so alkanes are **saturated**.
Here are a few examples of alkanes —


methane


ethane


propane


cyclohexane, C_6H_{12}

You get **cycloalkanes** too. They have a ring of carbon atoms with two hydrogens attached to each carbon. Cycloalkanes have two fewer hydrogens than other alkanes (assuming they have only one ring) so cycloalkanes have a different general formula from that of normal alkanes (C_nH_{2n}), but they are still saturated.

Rules of nomenclature

The IUPAC system for naming organic compounds is the agreed international language of chemistry. Years ago, organic compounds were given whatever names people fancied, such as acetic acid and ethylene. But these names caused confusion between different countries.

IUPAC (The International Union of Pure and Applied Chemistry) is a group founded in 1919 with the aim of creating international standards in Chemistry so that research could be shared more easily across the world. Amongst other things, this included making rules for naming organic molecules.

There are a few rules to learn before you meet any specific compounds.

1. Count the carbon atoms in the longest continuous chain to give you the stem.

Number of Carbon Atoms	Stem
1	*meth-*
2	*eth-*
3	*prop-*
4	*but-*
5	*pent-*
6	*hex-*
7	*hept-*
8	*oct-*
9	*non-*
10	*dec-*

Figure 2: *The stems for carbon chains up to ten carbon atoms long.*

Learning Objectives:

- Know that alkanes are saturated hydrocarbons that only contain single C–C and C–H bonds.
- Be able to use the IUPAC rules of nomenclature to systematically name organic compounds.

Specification Reference 4.1.1, 4.1.2

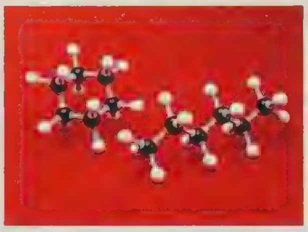
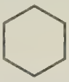


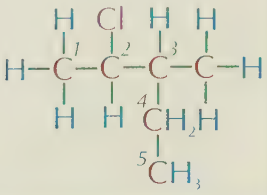
Figure 1: *Molecular models of cyclohexane (left) and hexane (right).*

Tip: The skeletal formula of cyclohexane looks like this:

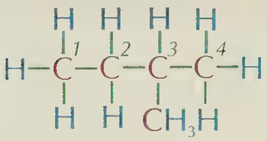


Tip: The IUPAC naming system may seem like a foreign language at the moment, but you'll get loads of practice at naming organic compounds during this Module.

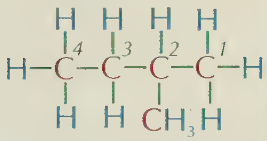
Tip: Be careful, the longest carbon chain may not be in a straight line:



Tip: Always number the longest continuous carbon chain so that the name contains the lowest numbers possible. For example, you could number this chain:



which would make it 3-methylbutane.
But you should actually number it in the opposite direction to get 2-methylbutane.



2. The main functional group of the molecule usually tells you what homologous series the molecule is in, and so gives you the prefix or suffix. For example, alcohols all have the suffix '-ol', and chloroalkanes have the prefix 'chloro-'. You'll learn the prefix or suffix for each homologous series as you meet them in this Module.
3. Number the longest carbon chain so that the main functional group has the lowest possible number. If there's more than one longest chain, pick the one with the most side-chains.
4. Any side-chains or less important functional groups are added as prefixes at the start of the name. Put them in alphabetical order, after the number of the carbon atom each is attached to.
5. If there's more than one identical side-chain or functional group, use di- (2), tri- (3) or tetra- (4) before that part of the name — but ignore this when working out the alphabetical order.

Naming alkanes

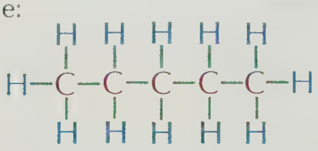
Alkanes are the simplest type of molecules to name. There are two types you need to learn to name — straight chain alkanes and branched chain alkanes.

Straight-chain alkanes

There are two parts to the name of a straight-chain alkane. The first part (the stem) states how many carbon atoms there are in the molecule. The second part is always "-ane". It's the "-ane" bit that lets people know it's an alkane.

Example

This molecule is pentane:



The stem is pent-, which tells you that the molecule has 5 carbons in it, and the -ane bit at the end tells you it's an alkane.

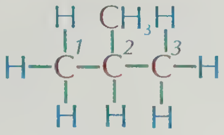
Branched alkanes

Branched alkanes have side chains. These are the carbon atoms that aren't part of the longest continuous chain. To name branched alkanes you first need to count how many carbon atoms are in the longest chain and work out the stem (just like you would for a straight-chain alkane). Once you've done that you can name the side chains. The side chains are named according to how many carbon atoms they have (see Figure 3) and which carbon atom they are attached to. If there's more than one side chain in a molecule, you place them in alphabetical order. So but- groups come before eth- groups which come before meth- groups.

Number of Carbon Atoms	Side Chain Prefix
1	*methyl-*
2	*ethyl-*
3	*propyl-*
4	*butyl-*
5	*pentyl-*
6	*hexyl-*

Figure 3: *Names of carbon side chains.*

Examples


2-methylpropane

The longest continuous carbon chain is 3 carbon atoms, so the stem is propane.

There's one side chain, which has one carbon atom so it's a methyl group.

It's joined to the main carbon chain at the 2nd carbon atom, so it's a 2-methyl group.

The alkane is called 2-methylpropane.

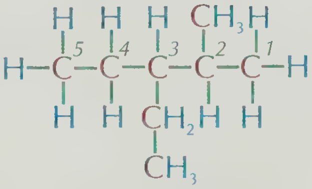
The longest continuous carbon chain is 5 carbon atoms, so the stem is pentane.

There are two side chains.

One side chain is a methyl group joined to the 2nd carbon atom: 2-methyl-.

The other is an ethyl group (2 carbons) joined to the 3rd carbon atom: 3-ethyl-.

Side chains go in alphabetical order, so the alkane is 3-ethyl-2-methylpentane.

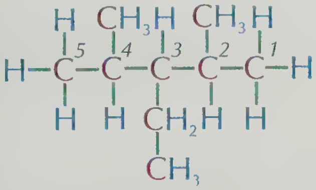

3-ethyl-2-methylpentane

Exam Tip
Always number each carbon on a drawing of your molecule — it makes it much easier to name molecules where there are lots of branches or functional groups.

Some alkanes have two or more of the same side chain. Remember that you just need to put a prefix before that part of the name to tell you how many of that side chain there are. You ignore these prefixes when putting the groups in alphabetical order (so 'dimethyl' would still come after 'ethyl').

Tip: When you're naming molecules commas are put between numbers (for example 2,2) and dashes are put between numbers and letters (for example 2-methyl).

Examples


3-ethyl-2,4-dimethylpentane

The longest carbon chain is five carbons, so the stem is pent-. You could choose two different routes to number the main chain — one way has three branches off the main chain, and the other way has two (see Figure 4).

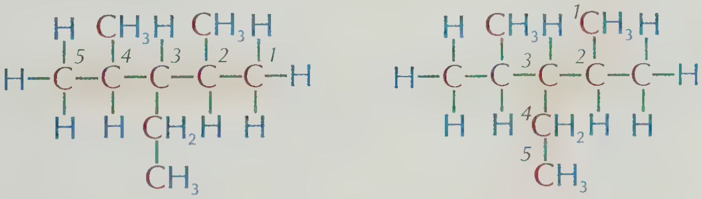


Figure 4: *Two possible ways of numbering the longest carbon chain in a molecule*

The numbering in the left hand diagram is correct — this way the main carbon chain has the most branches.

There are two methyl side chains, one attached to the second carbon and one attached to the fourth carbon, so there will be a 'dimethyl' prefix. There is also one ethyl group attached to the third carbon, so there'll also be an 'ethyl' prefix.

Side chains go in alphabetical order, ignoring any 'di' or 'tri' prefixes, so the molecule is 3-ethyl-2,4-dimethylpentane.

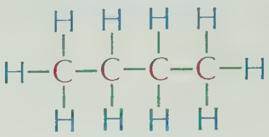
Tip: When you write down the numbers of the carbons that groups of the same type are attached to, you should write them in ascending order. So the molecule on the left is 3-ethyl-2,4-dimethylpentane, rather than 3-ethyl-4,2-dimethylpentane.

Exam Tip
If you're asked to name a molecule from its molecular formula, it can help to draw it out first.

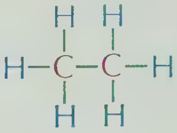
Practice Questions — Application

Q1 Name the alkanes shown below.

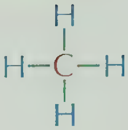
a)



b)



c)



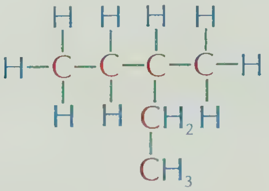
d) C_9H_{20}

e) C_7H_{16}

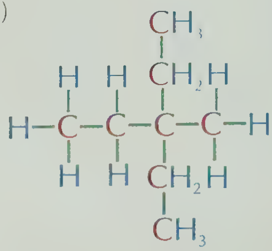
f) $C_{10}H_{22}$

Q2 Name the following branched alkanes:

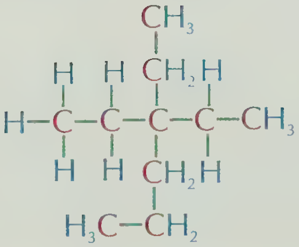
a)



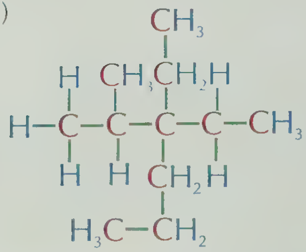
b)



c)



d)



Practice Questions — Fact Recall

Q1 What is an alkane?

Q2 Give the general formula for an alkane.

Q3 What is the stem for a carbon chain containing six carbon atoms?

Q4 What is the name for a carbon side chain containing two carbon atoms?

Q5 If there are two methyl- side chains what prefix should you add to methyl- when naming the molecule?

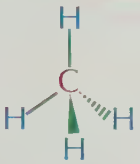
6. Properties of Alkanes

You need to know a little bit about the physical and chemical properties of the alkanes. Luckily for you, the next few pages happen to be about just that.

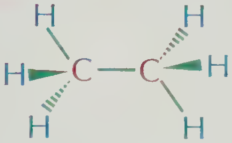
Shapes of alkane molecules

In an alkane molecule, each carbon atom has four pairs of bonding electrons around it. They all repel each other equally. So the molecule forms a **tetrahedral shape** around each carbon. The bond angles around each carbon will be 109.5°

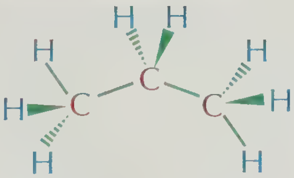
Examples — Maths Skills



Methane has one tetrahedral carbon.



Ethane has two tetrahedral carbons.



Propane has three tetrahedral carbons.

Bonding in alkanes

The C–C and C–H bonds in alkanes are all single covalent bonds. You can use the 'orbital overlap' model to explain how the bonds are formed. The model states that covalent bonds can form between two atoms if they're arranged so that the outer atomic orbitals overlap. The orbitals then combine to form a shared orbital that forms a bond between the atoms. How well the orbitals overlap determines how strong the bond is. In alkanes, atomic orbitals on carbon and hydrogen atoms are positioned so that they overlap to form a new, shared orbital lying directly between the bonded atoms. This type of covalent bond is called a sigma (σ-) bond.

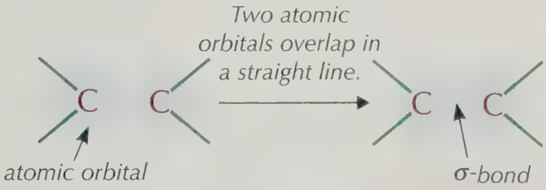


Figure 1: *The formation of a sigma (σ-) bond.*

The high electron density between the nuclei means there is a strong electrostatic attraction between the nuclei and the shared pair of electrons. This means that σ-bonds have a high bond enthalpy — they are the strongest type of covalent bonds. The bonded atoms are free to rotate around the σ-bond as whichever way the atoms point, the atomic orbitals between them will always overlap.

Reactivity of alkanes

Alkanes are pretty unreactive. They will combust with oxygen (see page 217), and undergo substitution reactions with highly reactive free radical species (see page 221), but that's about it.

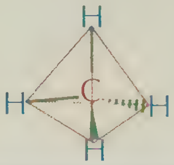
The low reactivity of alkanes can be explained by the bonding in alkane molecules. The C–C and C–H σ-bonds all have a large bond enthalpy, making them very strong and therefore difficult to break. The bonds are also non-polar. This means that they won't attract any positively or negatively charged particles to react with them.

Learning Objectives:

- Be able to explain the tetrahedral shape and bond angle around each carbon atom in alkanes in terms of electron pair repulsion.
- Know that the single bonds in alkanes are σ- (sigma) bonds which form from the overlap of orbitals directly between the bonding atoms.
- Know that atoms are able to rotate freely around σ-bonds.
- Be able to explain the low reactivity of alkanes with many reagents in terms of the high bond enthalpy and very low polarity of the σ-bonds present.
- Be able to explain the variations in boiling points of alkanes with different carbon-chain length and branching, in terms of induced dipole–dipole interactions.
- Describe the complete combustion of alkanes, as used in fuels, and the incomplete combustion of alkane fuels in a limited supply of oxygen with the resulting potential dangers from CO.

Specification Reference 4.1.2

Tip: If you draw lines joining up the Hs in tetrahedral molecules, you get a tetrahedron:



Tip: There's lots more about induced dipole-dipole interactions on pages 123-124.

Tip: Remember that when you boil or melt a small covalent compound, you're only breaking the intermolecular forces between molecules. The covalent bonds between the atoms within each molecule stay intact.

Figure 2: *The alkane propane is a gas at room temperature and pressure.*

Exam Tip
If you get a question on this in the exam, make sure you talk about the amount of surface contact and not just the surface area of the molecules — otherwise you might miss out on some marks.

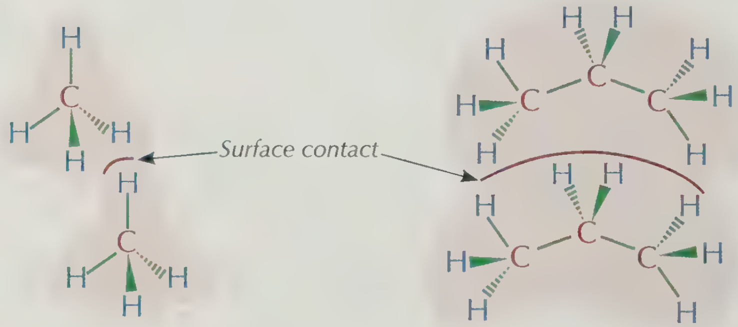
Boiling points of alkanes

The boiling point of an alkane depends on its size and shape. The smallest alkanes, like methane, are gases at room temperature and pressure — they've got very low boiling points. Larger alkanes are liquids — they have higher boiling points. This is due to differences in their intermolecular forces.

Alkanes have covalent bonds inside the molecules. Between the molecules, there are **induced dipole-dipole interactions** (also called London forces) which hold them all together (see pages 123-124). The longer the carbon chain, the more induced dipole-dipole interactions there are. This is because they have a larger molecular surface area so there is more surface contact between the molecules and there are more electrons to interact. So as the molecules get longer, it takes more energy to overcome the induced dipole-dipole interactions and separate them, and the boiling point rises.

Example

Methane is a very small molecule so there is little surface contact between the molecules. This means that the induced dipole-dipole interactions between the molecules are weak and the boiling point of methane is very low. Propane has a much higher boiling point because the molecules are much larger so have more surface contact with each other. Therefore, the induced dipole-dipole interactions between the molecules are stronger.



Methane
boiling point = −161 °C

Propane
boiling point = −42 °C

You can use your knowledge about the strength of induced dipole-dipole interactions to explain trends in boiling points of different sized alkanes.

Example **Maths Skills**

The boiling points of the first six alkanes are shown in Figure 3.

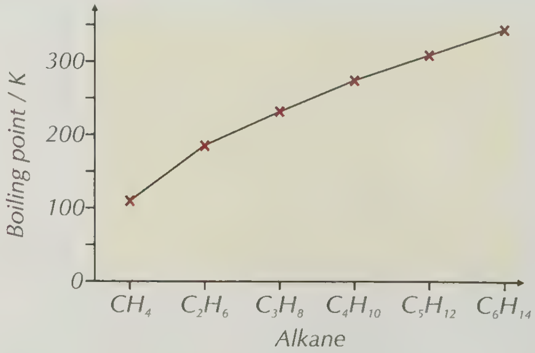


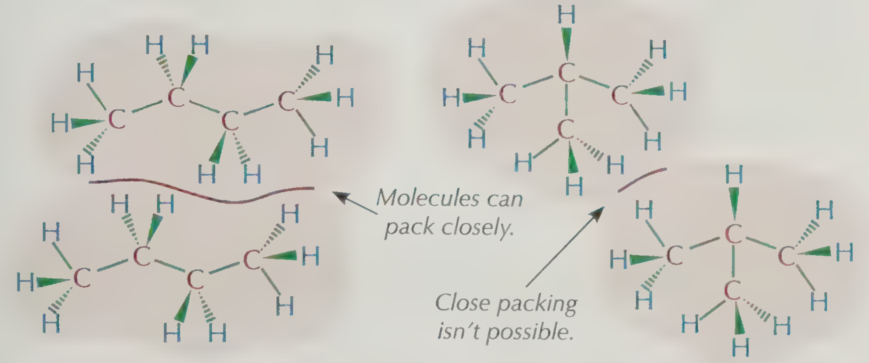
Figure 3: *The boiling points of the first six alkanes.*

As the alkane chains get longer, the number of electrons in the molecules and the surface contact between molecules increase. So the induced dipole-dipole interactions are stronger, and so the boiling points increase.

A branched-chain alkane has a lower boiling point than its straight-chain isomer. Branched-chain alkanes can't pack closely together and they have smaller molecular surface areas — so the induced dipole-dipole interactions are reduced.

Example

Butane and methylpropane are both isomers of C_4H_{10}. Butane has a higher boiling point than methylpropane because the molecules can pack closely together, therefore have more surface contact and so have more induced dipole-dipole interactions holding the molecules together.



Butane
boiling point = 0 °C

Methylpropane
boiling point = −12 °C

Tip: Butane and methylpropane are chain isomers — they've got the same molecular formula but their structural formulas are different.

Complete combustion of alkanes

If you burn (oxidise) alkanes with enough oxygen, you get carbon dioxide and water — this is a **complete combustion** reaction.

Examples

Here's the equation for the complete combustion of propane:

$$C_3H_{8(g)} + 5O_{2(g)} \rightarrow 3CO_{2(g)} + 4H_2O_{(g)}$$

This is the equation for the complete combustion of heptane:

$$C_7H_{16(g)} + 11O_{2(g)} \rightarrow 7CO_{2(g)} + 8H_2O_{(g)}$$

Tip: You only get complete combustion when there's loads of oxygen around. If oxygen is in short supply, you'll get incomplete combustion instead. There's more on incomplete combustion on the next page.

Complete combustion reactions happen between gases, so liquid alkanes have to be vaporised first. Smaller alkanes turn into gases more easily (they're more **volatile**), so they'll burn more easily too.

Alkanes and fuels

When alkanes burn, some energy is used to break the covalent bonds but more energy is released by forming the new product bonds in CO_2 and H_2O. This means that larger alkanes release more energy per mole than smaller alkanes, because more CO_2 and H_2O are formed. Because they release so much energy when they burn, alkanes make excellent fuels.

Examples

- Propane is used as a central heating and cooking fuel.
- Butane is bottled and sold as camping gas.
- Petrol and diesel are both made up of a mixture of alkanes too (and additives) — these are used as fuels for transport.

Figure 4: *A butane gas camping stove. The blue flame indicates that the combustion is complete.*

Identifying an unknown hydrocarbon

Complete combustion reactions happen between gases. All gases at standard temperature and pressure have the same molar volume — 24 dm^3. This means you can use the ratio of the volumes of gases reacting together to calculate the molar ratios, and then work out what hydrocarbon is combusting.

Example — **Maths Skills**

30 cm^3 of an unknown hydrocarbon, X, combusts completely with 240 cm^3 oxygen to form 150 cm^3 carbon dioxide. You can use this information to identify the molecular formula of X by following these steps:

- Using the volumes provided, a reaction equation can be written.

  $30X + 240O_2 \rightarrow 150CO_2 + ?H_2O$

- This can be simplified by dividing everything by 30.

  $X + 8O_2 \rightarrow 5CO_2 + nH_2O$

- All the oxygen atoms in molecules on the right-hand side of the equation come from the oxygen molecules on the left-hand side (none come from the hydrocarbon). You can use this fact to balance the oxygen atoms on the right-hand side of the equation, and so work out how much water is produced.

  8 moles of oxygen react to form 5 moles of carbon dioxide and *n* moles of water. So any oxygen atoms that don't end up in CO_2 must be in H_2O.

  This means that $n = (8 \times 2) - (5 \times 2) = \mathbf{6}$.

- Write down the reaction equation again, including your value for *n*.

  $X + 8O_2 \rightarrow 5CO_2 + 6H_2O$

- Now all you need to do to find the formula of X is to balance the left-hand side of the equation with the right-hand side.

  All the carbon atoms from X end up in carbon dioxide, and all the hydrogen atoms from X end up in water, so the number of carbon atoms in X is 5 and the number of hydrogen atoms in X is 12.

  The molecular formula of X is $\mathbf{C_5H_{12}}$.

Tip: Have look back at page 66 for more about balancing equations.

Tip: This method will give you the molecular formula of the hydrocarbon, but if that hydrocarbon forms isomers you won't know which isomer was used.

Incomplete combustion of alkanes

If there isn't much oxygen around, an alkane will still burn, but it will produce carbon monoxide and water. This is an **incomplete combustion** reaction.

Examples

Here's the reaction that occurs when methane is burnt in a limited supply of oxygen:

$$2CH_{4(g)} + 3O_{2(g)} \rightarrow 2CO_{(g)} + 4H_2O_{(g)}$$

And here's the equation for the incomplete combustion of ethane:

$$2C_2H_{6(g)} + 5O_{2(g)} \rightarrow 4CO_{(g)} + 6H_2O_{(g)}$$

Tip: Not all incomplete combustion reactions will only produce water and carbon monoxide. Some will produce particulate carbon or small amounts of carbon dioxide as well. Just make sure your equation balances and you should be fine.

Carbon monoxide poisoning

Incomplete combustion is a problem because carbon monoxide is poisonous. The oxygen in your bloodstream is carried around by haemoglobin. Carbon monoxide is better at binding to haemoglobin than oxygen is. So if you breathe in air with a high concentration of carbon monoxide it will bind to the haemoglobin in your bloodstream before the oxygen can. This means that less oxygen will reach your cells. You will start to suffer from symptoms associated with oxygen deprivation — things like fatigue, headaches, and nausea. At very high concentrations, carbon monoxide can even be fatal.

Any appliance that burns alkanes can produce carbon monoxide. This includes things like gas- or oil-fired boilers and heaters, gas stoves, and coal or wood fires. Cars also produce carbon monoxide. All appliances that use an alkane-based fuel need to be properly ventilated. They should be checked and maintained regularly, and their sources of ventilation should never be blocked. If you have any alkane burning appliances it's a good idea to have a carbon monoxide detector around.

Tip: Carbon monoxide is a colourless, odourless gas. This makes it very dangerous because you don't know it's there until it's too late.

Figure 5: *A carbon monoxide detector.*

Practice Questions — Application

Q1 Propane (C_3H_8) and octane (C_8H_{18}) are both alkanes.

a) Explain why octane has a higher boiling point than propane.

b) Write equations for the complete and incomplete combustion of octane.

Q2 Pentane and 2,2-dimethylpropane both have the molecular formula C_5H_{12}. Which has the higher boiling point? Explain your answer.

Q3 20 cm^3 of an unknown hydrocarbon burns completely in 130 cm^3 oxygen to produce 80 cm^3 CO_2. What is the molecular formula of the unknown hydrocarbon?

Practice Questions — Fact Recall

Q1 Describe the molecular shape around each carbon atom in an alkane.

Q2 Describe how a σ-bond is formed.

Q3 Name two factors that affect the boiling point of an alkane.

Q4 What are the products of the complete and incomplete combustion of alkanes?

Q5 Explain why carbon monoxide is poisonous.

7. Bond Fission

Before you go on to meet more organic reactions, you need to know a bit about the different types of bond fission and how the breaking and forming of bonds can be shown using reaction mechanisms. Here's a quick summary...

Learning Objectives:

- Be able to describe heterolytic fission in terms of one bonding atom receiving both electrons from the bonded pair.
- Be able to describe homolytic fission in terms of each bonding atom receiving one electron from the bonded pair, forming two radicals.
- Be able to describe a radical as a species with an unpaired electron and use 'dots' to represent species that are radicals in mechanisms.
- Know that a 'curly arrow' describes the movement of an electron pair and can show either heterolytic fission or formation of a covalent bond.
- Know how to write reaction mechanisms, using diagrams, to show clearly the movement of an electron pair with 'curly arrows' and relevant dipoles.

Specification Reference 4.1.1

Homolytic and heterolytic bond fission

Breaking a covalent bond is called **bond fission**. A single covalent bond is a shared pair of electrons between two atoms. It can break in two ways.

Heterolytic fission

In heterolytic fission the bond breaks unevenly with one of the bonded atoms receiving both electrons from the bonded pair. Two different substances are formed — a positively charged cation (X^+), and a negatively charged anion (Y^-). The general equation for heterolytic fission is:

$$XY \rightarrow X^+ + Y^-$$

Homolytic fission

In homolytic fission, the bond breaks evenly and each bonding atom receives one electron from the bonded pair. Two electrically uncharged **radicals** are formed. Radicals are particles that have an unpaired electron.
The unpaired electron is shown by a dot after the radical. The general equation for homolytic fission is:

$$XY \rightarrow X\cdot + Y\cdot$$

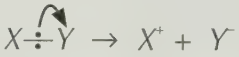
Because of the unpaired electron, these radicals are very reactive.

Reaction mechanisms

Reactions occur via a series of different processes. These processes can be shown step by step using a reaction mechanism. Reaction mechanisms use curly arrows to show the movement of electrons during a reaction. A curly arrow (↷) shows the movement of a pair of electrons. You can use curly arrows to show how covalent bonds are broken.

Example

During heterolytic fission a pair of electrons shared in a covalent bond moves onto one of the species, giving it a negative charge. This leaves the other species with a positive charge.



Curly arrows show the movement of a pair of electrons.

Reaction mechanisms come up a lot in chemistry — it's much easier to explain what's happening in a reaction by drawing diagrams than by using words.

Tip: You can use filled in arrows (like this: —►) or line arrows (like this: →) to show the movement of an electron pair. They mean the same thing.

Tip: There are lots of reaction mechanisms using curly arrows on pages 230-234.

Practice Questions — Fact Recall

Q1 What is bond fission?

Q2 a) Name the two different types of bond fission.
b) Describe how the two different types of bond fission are different.

Q3 What is a radical?

Q4 In a reaction mechanism, how do you show that a particle is a radical?

Q5 What do curly arrows show?

8. Substitution Reactions

A substitution reaction is a reaction where an atom in a compound gets swapped with another atom. This section is all about how haloalkanes can be formed by substituting a hydrogen in an alkane with a halogen.

Formation of haloalkanes

Haloalkanes are formed when halogens react with alkanes in photochemical reactions. **Photochemical reactions** are reactions that are started by light. During the formation of haloalkanes a hydrogen atom is substituted (replaced) by a halogen such as chlorine or bromine in a **radical substitution reaction**.

There are lots of reactions between halogens and alkanes to form different haloalkanes, but one of the most industrially important free radical substitution reactions is the synthesis of chloromethane.

Synthesis of chloromethane

A mixture of methane and chlorine will not react on its own but when exposed to UV light it reacts with a bit of a bang to form chloromethane. The overall equation for this reaction is shown below.

$$CH_4 + Cl_2 \xrightarrow{UV} CH_3Cl + HCl$$

The reaction mechanism for the synthesis of chloromethane by a photochemical reaction has three stages — initiation, propagation and termination.

Initiation

In the initiation step, radicals are produced. Sunlight provides enough energy to break some of the Cl–Cl bonds — this is **photodissociation**.

$$Cl_2 \xrightarrow{UV} 2Cl\bullet$$

The bond splits equally and each atom gets to keep one electron (homolytic fission). These atoms are highly reactive radicals, $Cl\bullet$, because each one has an unpaired electron.

Propagation

During propagation, radicals are used up and created in a chain reaction. First, $Cl\bullet$ attacks a methane molecule:

$$Cl\bullet + CH_4 \rightarrow CH_3\bullet + HCl$$

The new methyl radical, $CH_3\bullet$, can then attack another Cl_2 molecule:

$$CH_3\bullet + Cl_2 \rightarrow CH_3Cl + Cl\bullet$$

The new $Cl\bullet$ can attack another CH_4 molecule, and so on, until all the Cl_2 or CH_4 molecules are used up.

Termination

In the termination step, radicals are mopped up. If two radicals join together, they make a stable molecule — this terminates the chain reaction. Many radical chain reactions have heaps of possible termination reactions. Here are some from the synthesis of chloromethane, there are three:

$$CH_3\bullet + Cl\bullet \rightarrow CH_3Cl \qquad CH_3\bullet + CH_3\bullet \rightarrow C_2H_6 \qquad Cl\bullet + Cl\bullet \rightarrow Cl_2$$

Learning Objectives:

- Be able to describe the reaction of alkanes with Cl_2 and Br_2 by radical substitution using ultraviolet radiation, including a mechanism involving homolytic fission and radical reactions in terms of initiation, propagation and termination.
- Understand the limitations of radical substitution in synthesis due to the formation of a mixture of organic products, in terms of further substitution and reactions at different positions in a carbon chain.

Specification Reference 4.1.2

Tip: The reaction between bromine and methane works in the same way as the reaction between chlorine and methane — you just swap Cl for Br. The overall equation is then:

$$CH_4 + Br_2 \xrightarrow{UV} CH_3Br + HBr$$

The mechanism is exactly the same too.

Exam Tip

When you write radical equations, make sure that there are the same number of radicals on each side (or that two radicals are combining to create a non-radical).

Problems with radical substitution

The big problem with radical substitution if you're trying to make a particular product is that you don't only get the product you're after, but a mixture of products. For example, if you're trying to make chloromethane, and there's too much chlorine in the reaction mixture, some of the remaining hydrogen atoms on the chloromethane molecule will be swapped for chlorine atoms. The propagation reactions happen again, this time to make dichloromethane (CH_2Cl_2):

$$Cl\bullet + CH_3Cl \rightarrow CH_2Cl\bullet + HCl$$
$$CH_2Cl\bullet + Cl_2 \rightarrow CH_2Cl_2 + Cl\bullet$$

It doesn't stop there. Another substitution reaction can take place to form trichloromethane ($CHCl_3$):

$$Cl\bullet + CH_2Cl_2 \rightarrow CHCl_2\bullet + HCl$$
$$CHCl_2\bullet + Cl_2 \rightarrow CHCl_3 + Cl\bullet$$

Tetrachloromethane (CCl_4) is formed in the last possible substitution. There are no more hydrogens attached to the carbon atom, so the substitution process has to stop. So the end product is a mixture of CH_3Cl, CH_2Cl_2, $CHCl_3$ and CCl_4. This is a nuisance, because you have to separate the chloromethane from the other three unwanted by-products.

The best way of reducing the chance of these by-products forming is to have an excess of methane. This means there's a greater chance of a chlorine radical colliding only with a methane molecule and not a chloromethane molecule.

Another problem with radical substitution is that it can take place at any point along the carbon chain. So a mixture of isomers can be formed. For example, reacting propane with chlorine will produce a mixture of 1-chloropropane and 2-chloropropane.

Tip: Some of the products formed in the termination step will be trace impurities in the final sample.

Tip: You get exactly the same problem with any radical substitution reaction — there's always a mixture of products, which is really annoying if you're trying to make a particular haloalkane.

Practice Questions — Application

Q1 Bromine reacts with methane to form bromomethane in a three-stage reaction mechanism.

a) Give the names of the three stages of this reaction mechanism.

b) Write equations to show what happens at each of these stages.

c) What other products besides bromomethane are likely to be in the reaction mixture?

Q2 Ethane (C_2H_6) reacts with chlorine to form chloroethane (C_2H_5Cl).

a) What name is given to the mechanism for this reaction?

b) Describe this reaction mechanism.

c) This reaction gives a mixture of products. How could the concentration of chloroethane in the final mixture be increased?

Practice Questions — Fact Recall

Q1 Write an equation for the production of chloromethane from chlorine and methane.

Q2 What type of fission occurs in the initiation step of a free radical substitution reaction?

Q3 Give two reasons why a mixture of products is formed during free radical substitution reactions.

Exam Tip

If you're asked to describe a mechanism, you don't have to write out a really long wordy answer — you can use equations to help you describe a particular step in the reaction.

9. Alkenes and their Properties

The alkenes are another group of hydrocarbons. They're really similar to alkanes but they contain a carbon-carbon double bond. This topic is all about alkenes and how to name them.

Learning Objectives:

- Be able to use the IUPAC rules of nomenclature to systematically name alkenes.
- Know that alkenes are unsaturated hydrocarbons containing a C=C bond.
- Know that a C=C bond comprises a π-bond and a σ-bond and that there is restricted rotation of the π-bond.
- Be able to explain the reactivity of alkenes in terms of the relatively low bond enthalpy of the π-bond.
- Be able to explain the trigonal planar shape and bond angle around each carbon in the C=C of alkenes in terms of electron pair repulsion.

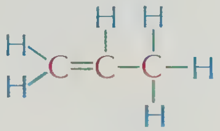
Specification Reference 4.1.1, 4.1.3

What are alkenes?

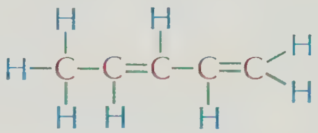
Alkenes have the general formula C_nH_{2n}. They're just made of carbon and hydrogen atoms, so they're hydrocarbons. Alkene molecules all have at least one C=C double covalent bond. Molecules with C=C double bonds are **unsaturated** because they can make more bonds with extra atoms in addition reactions.

Examples

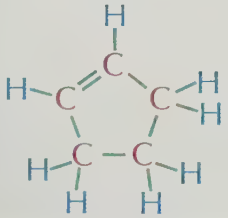
Here are a few pretty diagrams of alkenes:



propene



penta-1,3-diene



cyclopentene

A cyclic alkene has two fewer hydrogen atoms than an open-chain alkene. Carbons can only have four bonds — a double bond means that the carbons can make one less bond with a hydrogen.

Naming alkenes

Alkenes are named in the same way as alkanes (see pages 211-213), but the -ane ending is changed to an -ene ending — see Figure 2.

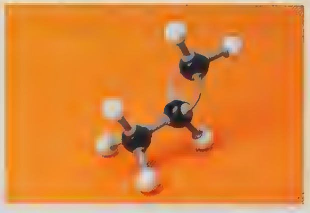


Figure 1: *A molecular model of propene.*

No. of Carbon Atoms	Stem	Alkene
2	*eth-*	*ethene* (C_2H_4)
3	*prop-*	*propene* (C_3H_6)
4	*but-*	*butene* (C_4H_8)
5	*pent-*	*pentene* (C_5H_{10})
6	*hex-*	*hexene* (C_6H_{12})

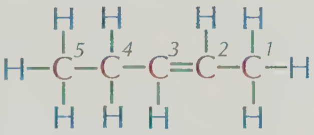
Figure 2: *Naming some alkenes.*

For alkenes with more than three carbons, you need to say which carbon the double bond starts from.

Example

The longest chain is 5 carbons, so the stem of the name is pent-.

The functional group is C=C, so it's pentene. Number the carbons from right to left (so the double bond starts on the lowest possible number). The first carbon in the double bond is carbon 2. So this molecule is pent-2-ene.



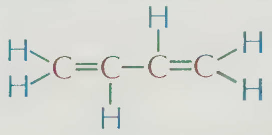
pent-2-ene

Tip: When you're naming alkenes the stem is based on the longest continuous carbon chain containing a double bond — even if there is a carbon chain that is longer.

If the alkene has two double bonds the suffix becomes diene. The stem of the name usually gets an extra 'a' too (e.g. buta-, penta-, not but-, pent-) when there's more than one double bond. And you might see the numbers written first.

Tip: If there is more than one double bond in a molecule the stem is based on the longest continuous carbon chain that contains the most double bonds — even if there are longer carbon chains.

Example



This molecule can be named as buta-1,3-diene or 1,3-butadiene.

Structure of a double bond

A double bond is made up of a **sigma (σ-) bond** and a **pi (π-) bond**. The σ-bond is formed in the same way as it is in alkanes (see page 215) — two orbitals overlap in a straight line which gives the highest possible electron density between the two nuclei (see Figure 3). This is a single covalent bond.

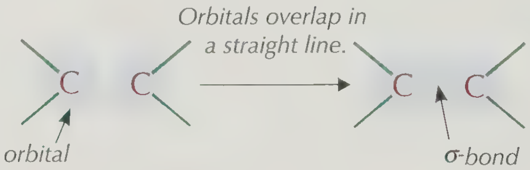


Figure 3: *The formation of a sigma (σ-) bond.*

Tip: Don't get confused between sigma and pi bonds. Just remember, sigma bonds are the same as covalent single bonds. Pi bonds involve p orbitals.

A π-bond is formed when two p orbitals overlap sideways. It's got two parts to it — one 'above' and one 'below' the molecular axis. This is because the p orbitals which overlap are dumb-bell shaped — see Figure 4.

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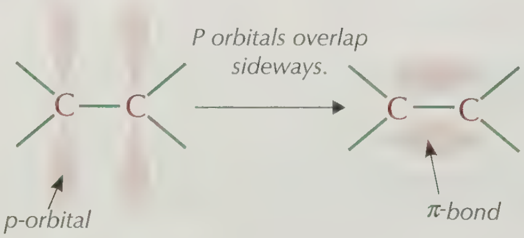


Figure 4: *The formation of a pi (π-) bond.*

Exam Tip
If you're asked to describe a sigma or a pi bond in the exam, you can draw a diagram — just make sure you label it properly.

π-bonds are weaker than σ-bonds because the electron density is spread out above and below the nuclei. This means that the electrostatic attraction between the nuclei and the shared pair of electrons is weaker, so π-bonds have a relatively low bond enthalpy. This means that a double bond (π-bond + σ-bond) is not twice as strong as a single bond (just a σ-bond).

Tip: This explains why the average bond enthalpy of a C=C double bond (+612 kJ mol^{-1}) is not twice the average bond enthalpy of a C–C single bond (+347 kJ mol^{-1}). See page 168 for more on bond enthalpies.

Reactivity of the alkenes

Each double bond in an alkene is a bit like a hot dog. The π-bond is the bun and the σ-bond is sandwiched in the middle like the sausage — see Figure 5.

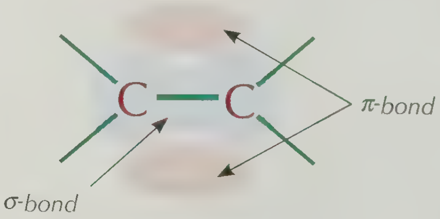


Figure 5: *Structure of a double bond.*

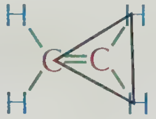
Because there are two pairs of electrons in the bond, the C=C double bond has a really high electron density. This makes alkenes pretty reactive. Another reason for the high reactivity is that the π-bond sticks out above and below the rest of the molecule. So, the π-bond is likely to be attacked by particles that have a low electron density and can accept a pair of electrons — these particles are called **electrophiles**. The low bond enthalpy of the π-bond also contributes to the reactivity of alkenes. Because the double bond's so reactive, alkenes are handy starting points for making other organic compounds and for making petrochemicals (organic compounds made from petroleum).

Tip: See page 230 for more on electrophiles.

Tip: Because of the double bond, alkenes are much more reactive than alkanes, which don't contain a double bond.

Double bond rotation

Carbon atoms in a C=C double bond and the atoms bonded to these carbons all lie in the same plane (they're planar). The three bonds repel each other as much as possible and arrange themselves into a trigonal planar shape — the atoms attached to each double-bond carbon are at the corners of an imaginary equilateral triangle — see Figure 6.



The bond angles in the planar unit are all 120°.

***Figure 6:** The trigonal planar shape around each carbon of C=C bonds in alkenes.*

Ethene, C_2H_4 (as in Figure 6) is completely planar, but in larger alkenes, only the >C=C< unit is planar.

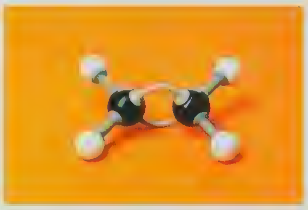
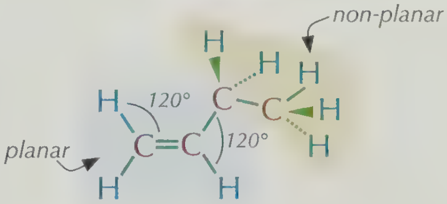


***Figure 7:** A molecular model of ethene. All of the atoms are in the same plane.*

Example

This molecule is but-1-ene. The carbon-carbon double bond section of the molecule is planar and the carbon-carbon single bond section is non-planar.

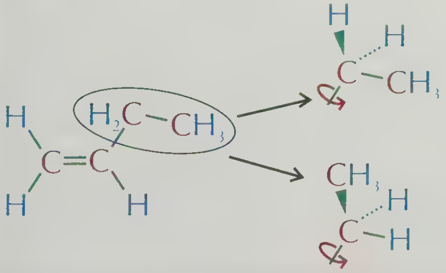


Tip: The C–C single bond section isn't planar because the bonding electron pairs repel each other giving a tetrahedral shape. The bond angles in a tetrahedral molecule are 109.5°.

Another important thing about C=C double bonds is that atoms can't rotate around them like they can around single bonds. This is because the p orbitals have to stay in the same position to overlap and form a π-bond. Double bonds are also fairly rigid — they don't bend much. Even though atoms can't rotate about the double bond, things can still rotate about any single bonds in the molecule.

Tip: See pages 116-119 for loads more about the shapes of molecules.

Example



In this molecule of but-1-ene the single C–C bond can rotate.

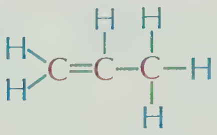
The restricted rotation around the C=C double bond is what causes alkenes to form stereoisomers (see page 227).

Exam Tip
When you're naming molecules in the exam always, always, always double-check what you've written. Accidentally writing -ane instead of -ene could cost you valuable marks.

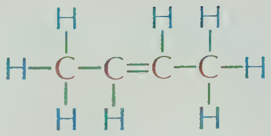
Practice Questions — Application

Q1 Name the alkenes below:

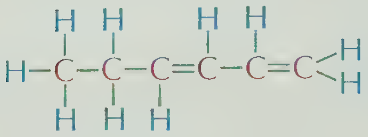
a)



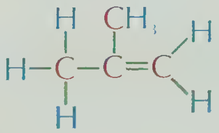
b)



c)



d)



Q2 Propene is more reactive than propane. Explain why.

Q3 The table below shows the average bond enthalpies of single and double carbon-carbon bonds:

Type of bond	Average bond enthalpy (kJ mol^{-1})
C–C	+347
C=C	+612

Using your knowledge of the structure of C=C double bonds, explain why the average bond enthalpy of a C=C double bond is not twice as large as that of a C–C single bond.

Practice Questions — Fact Recall

Q1 What is the general formula of an alkene?

Q2 a) Draw a diagram to show how a sigma bond is formed.

b) Draw a diagram to show how a pi bond is formed.

Q3 Are C=C double bonds susceptible to attack by nucleophiles or electrophiles?

Q4 a) What does the term trigonal planar mean?

b) Which part of an alkene molecule is trigonal planar?

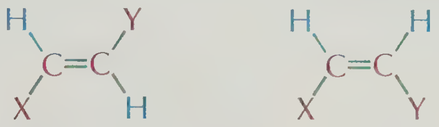
10. Stereoisomers

Structural isomers aren't the only isomers you need to know about. You also need to know all about stereoisomers... which is what this topic is about.

E/*Z* isomerism

Stereoisomers have the same structural formula but a different arrangement in space. Some alkenes have stereoisomers — this is because there's a lack of rotation around the C=C double bond. When the double-bonded carbon atoms each have two different atoms or groups attached to them, you get an '*E*-isomer' and a '*Z*-isomer'.

Each of the groups linked to the double-bonded carbons is given a priority. If the two carbon atoms have their 'higher priority groups' on opposite sides, then it's an *E*-isomer. If the two carbon atoms have their 'higher priority groups' on the same side, then it's a *Z*-isomer — see Figure 1.

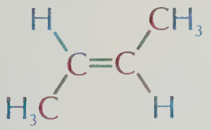


***E*-isomer** ***Z*-isomer**

Figure 1: *E-isomers and Z-isomers.*
In these diagrams X and Y are the higher priority groups.

Examples — Maths Skills

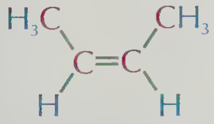
The double-bonded carbon atoms in but-2-ene (C_4H_8) each have an H and a CH_3 group attached. H groups are always the lowest priority, so the CH_3 groups on each of the carbons will be the highest priority.



E-isomer

When the CH_3 groups are across the double bond then it's the *E*-isomer.

This molecule is *E*-but-2-ene.

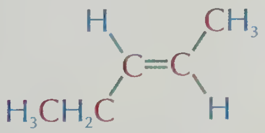


Z-isomer

When the CH_3 groups are both above or both below the double bond then it's the *Z*-isomer.

This molecule is *Z*-but-2-ene.

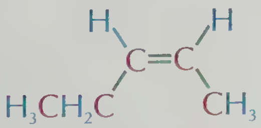
In pent-2-ene (C_5H_{10}) one of the double-bonded carbon atoms has an H and a CH_3 group attached to it. The other has an H and a CH_2CH_3 group attached.



E-isomer

The high priority groups (CH_3 and CH_2CH_3) are across the double bond so it's the *E*-isomer.

This molecule is *E*-pent-2-ene.



Z-isomer

The high priority groups are both below the double bond so it's the *Z*-isomer.

This molecule is *Z*-pent-2-ene.

Learning Objectives:

- Be able to define stereoisomers as compounds with the same structural formula but with a different arrangement in space.
- Be able to describe *E*/*Z* isomerism as an example of stereoisomerism, in terms of restricted rotation about a double bond and the requirement for two different groups to be attached to each carbon atom of the C=C group.
- Be able to use the Cahn–Ingold–Prelog (CIP) priority rules to identify the *E* and *Z* stereoisomers.
- Be able to describe cis-trans isomerism as a special case of *E*/*Z* isomerism in which two of the substituent groups attached to each carbon atom of the C=C group are the same.
- Be able to determine the possible E/Z or cis–trans stereoisomers of an organic molecule, given its structural formula.

Specification Reference 4.1.3

Tip: See page 225 for more about why double bonds can't rotate.

Tip: In alkanes, the groups are free to rotate around the single C-C bonds, so they don't form *E*/*Z* isomers.

Cahn-Ingold-Prelog priority rules

When the carbons on either end of a double bond both have the same groups attached, then it's easy to work out which is the *E*-isomer and which is the *Z*-isomer (like in the example on the last page). It only starts to get problematic if the carbon atoms both have totally different groups attached. Fortunately, three clever people (Mr Cahn, Mr Ingold and Mr Prelog) came up with a solution to this problem. Using the **Cahn-Ingold-Prelog (CIP) rules** you can work out which is the *E*-isomer and which is the *Z*-isomer for any alkene. They're really simple, and they work every time.

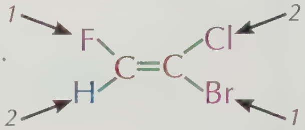
Figure 2: *Sir Christopher Ingold was one of the Chemists who developed the Cahn-Ingold-Prelog priority rules.*

The highest priority group on each of the $C=C$ carbons is the one which has the atom with the highest atomic number directly bonded to the carbon atom. If the higher priority groups on each of the $C=C$ atoms are positioned on the same side of the double bond, then the molecule is the *Z*-isomer, and if they're on opposite sides then it's the *E*-isomer.

Tip: If the two groups connected to one of the double-bonded carbons in an alkene are the same, then it won't have *E*/*Z* isomers. So neither propene nor but-1-ene have *E*/*Z* isomers. Try drawing them out if you're not sure.

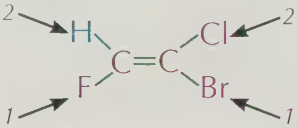
Example — Maths Skills

The molecule on the right shows one of the stereoisomers of 1-bromo-1-chloro-2-fluoroethene. The atoms directly attached to carbon-1 are bromine and chlorine. Bromine has an atomic number of 35 and chlorine has an atomic number of 17. So bromine is the higher priority group. The atoms directly attached to carbon-2 are fluorine and hydrogen. Fluorine has an atomic number of 9 and hydrogen has an atomic number of 1. So fluorine is the higher priority group.



In this stereoisomer of 1-bromo-1-chloro-2-fluoroethene, the higher priority groups (bromine and fluorine) are positioned across the double bond from one another. So it's the ***E*-isomer**.

In the *Z*-isomer, the higher priority groups are positioned on the same side of the double bond:



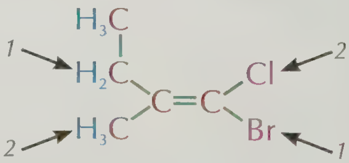
Exam Tip

An easy way to remember which isomer is which is to remember that in the *Z*-isomer, the groups are on 'ze zame zide', but in the *E*-isomer, they are 'enemies'.

Sometimes, the atoms directly bonded to the carbon are the same. For example, a methyl group and an ethyl group both have a carbon atom directly bonded to the $C=C$ carbon. If this is the case then you have to look at the next atom along in each group to work out which has the higher priority.

Example — Maths Skills

In the isomer of 1-bromo-1-chloro-2-methylbut-1-ene shown below, the atoms directly attached to carbon-1 are bromine and chlorine. Bromine has an atomic number of 35 and chlorine has an atomic number of 17. So bromine is the higher priority group.

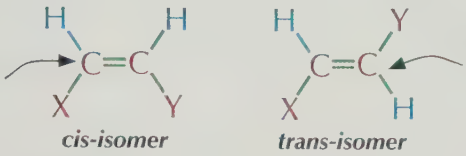


Meanwhile, carbon-2 is directly bonded to two carbon atoms, so you need to go further along the chain to work out the ordering. The methyl carbon is only attached to hydrogen atoms, but the ethyl carbon is attached to another carbon atom. So the ethyl group is higher priority. The higher priority groups (ethyl and bromine) are positioned across the double bond from one another. So it's the ***E*-isomer**.

Cis-trans isomerism

***Cis-trans* isomerism** is a special type of *E/Z* isomerism where the two carbon atoms either side of the double bond have at least one group in common. The cis-isomer is the one that has the two identical groups on the same side of the C=C double bond. The *trans*-isomer is the one that has the two identical groups on opposite sides of the C=C double bond — see Figure 4.

Tip: Because *cis-trans* isomerism is a type of *E/Z* isomerism, any molecule that shows *cis-trans* isomerism will also show *E/Z* isomerism.



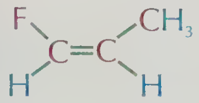
The identical hydrogen groups are on the same side of the double bond.

The identical hydrogen groups are on opposite sides of the double bond.

Figure 4: *Cis-isomers and trans-isomers.*

Example

This is *cis*-1-fluoropropene:



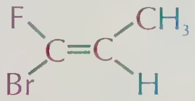
1-fluoropropene shows *cis-trans* isomerism because both of the carbons around the double bond have a hydrogen atom and another group (F or CH_3) attached to them.

Tip: To remember which is the *trans*-isomer and which is the *cis*-, it can be helpful to remember that the trans-Siberian railway goes across Siberia — so in the *trans*-isomer the same groups are across the double bond. And in the cis isomer, the same groups are on the same side.

You can't use the *cis-trans* system if there are more than two different groups (other than hydrogen atoms) attached around the double bond because you can't tell which isomer is which.

Example

Here is the structure of 1-bromo-1-fluoropropene:



1-bromo-1-fluoropropene has more than two different groups (other than hydrogen atoms) attached around the double bond. As a result the *cis–trans* system doesn't work. The *E/Z* system keeps on working though. In the *E/Z* system, Br has a higher priority than F, so the names depend on where the Br atom is in relation to the CH_3 group (which has a higher priority than the H atom).

Tip: If all this isomer stuff is a bit confusing, try to get your hands on a molecular modelling kit and have a go making the isomers yourself — it should make it all a bit clearer.

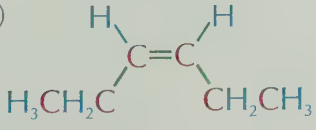
Practice Questions — Application

Q1 For each of the molecules below, state if it is:

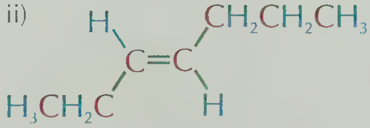
a) an *E*-isomer or a *Z*-isomer.

b) a *cis*-isomer or a *trans*-isomer.

i)



ii)



Q2 Draw the two stereoisomers of 3-methylhex-2-ene and label which is the *E*-isomer and which is the *Z*-isomer.

11. Reactions of Alkenes

Learning Objectives:

- Be able to define and use the term electrophile as an electron pair acceptor.
- Know the mechanism of electrophilic addition in alkenes by heterolytic fission.
- Be able to describe the addition reactions of alkenes with:

  (i) hydrogen in the presence of a suitable catalyst, e.g. Ni, to form alkanes.

  (ii) halogens to form dihaloalkanes, including the use of bromine to detect the presence of a double C=C bond as a test for unsaturation in a carbon chain (PAG 7).

  (iii) steam in the presence of an acid catalyst, e.g. H_3PO_4, to form alcohols.

  (iv) hydrogen halides to form haloalkanes.
- Be able to use Markownikoff's rule to predict formation of a major organic product in addition reactions of H–X to unsymmetrical alkenes, in terms of the relative stabilities of carbocation intermediates in the mechanism.

Specification Reference 4.1.3

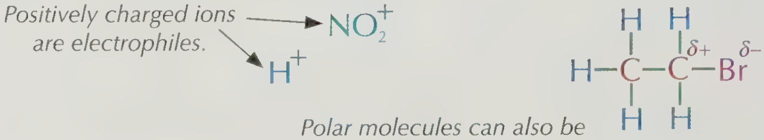
Remember those alkenes from page 223 — well they're back and this time they're reacting.

Electrophilic addition reactions

Electrophilic addition reactions aren't too complicated. The double bond in an alkene opens up and atoms are added to the carbon atoms. Electrophilic addition reactions happen because the double bond has got plenty of electrons and is easily attacked by **electrophiles**. Electrophiles are electron pair acceptors — they're usually a bit short of electrons, so they're attracted to areas where there's lots of them about.

Examples

Here are a few examples of electrophiles.



Positively charged ions are electrophiles.

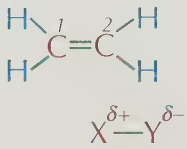
Polar molecules can also be electrophiles — the δ+ atom is attracted to places with lots of electrons.

The double bond is also nucleophilic — it's attracted to places that don't have enough electrons.

Tip: A nucleophile is an electron pair donor.

You need to learn the mechanism for electrophilic addition. Here is the general electrophilic addition reaction equation, using ethene as an example:

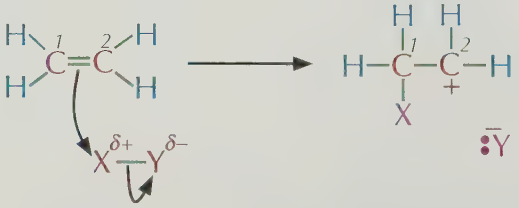
$$H_2C{=}CH_2 + X\text{–}Y \rightarrow CH_2XCH_2Y$$



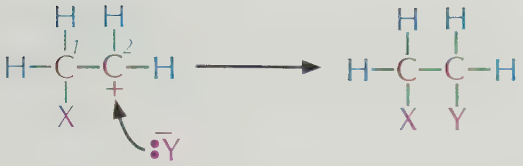
The carbon-carbon double bond repels the electrons in the X–Y bond, which polarises the X–Y bond (or the bond could already be polar, like in HBr).

Two electrons from the carbon-carbon double bond attack the δ+ X atom, creating a new bond between carbon 1 and the X atom. The X–Y bond breaks (heterolytic fission) and the electrons from the bond are taken by the Y atom to form a negative ion with a lone pair of electrons. Carbon 2 is left electron deficient — when the double bond was broken carbon 1 took the electrons to form a bond with the X atom, which left carbon 2 as a positively charged **carbocation** intermediate.

Tip: A carbocation is an organic ion containing a positively charged carbon atom.



The Y^- ion then acts as a **nucleophile**, attacking the positively charged carbocation intermediate, donating its lone pair of electrons and forming a new bond with carbon 2.



So overall, the X–Y molecule has been added to the alkene across the double bond to form a saturated compound.

Producing alkanes

Alkenes react with hydrogen gas to produce alkanes. The reaction needs a catalyst and a high temperature though. For example, ethene will react with hydrogen gas and a nickel catalyst at 150 °C to produce ethane. Here's the equation for the reaction:

$$H_2C{=}CH_2 + H_2 \xrightarrow[150\ °C]{Ni} CH_3CH_3$$

Reactions with halogens

Alkenes react with halogens to form dihaloalkanes. The halogens add across the double bond, and each of the carbon atoms ends up bonded to one halogen atom. It's an electrophilic addition reaction. The general reaction, using ethene as an example, is:

$$H_2C{=}CH_2 + X_2 \rightarrow CH_2XCH_2X$$

The mechanism for the reaction is shown below. Bromine is used as an example, but chlorine and iodine react in the same way.

Example

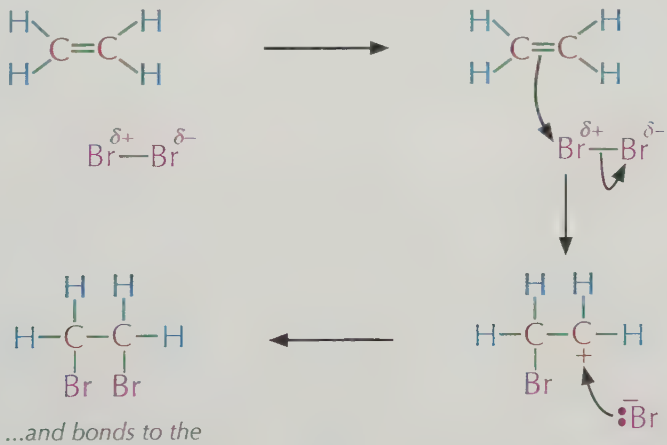
When you shake ethene with orange bromine water, the solution turns from orange to colourless. Here's the equation for this reaction:

$$H_2C{=}CH_2 + Br_2 \rightarrow CH_2BrCH_2Br$$

Here's the mechanism...

The double bond repels the electrons in Br_2, polarising Br–Br. This is called an induced dipole.

Heterolytic (unequal) fission of Br_2. The closer Br gives up its bonding electrons to the other Br and bonds to the C atom.



You get a positively charged carbocation intermediate. The Br^- now zooms over...

...and bonds to the other C atom, forming 1,2-dibromoethane.

Exam Tip

You must draw the curly arrows coming from the lone pair of electrons or from the bond. If you don't — you won't get all the marks for the mechanism in the exam.

Figure 1: *Unsaturated vegetable oils are reacted with hydrogen to form margarine.*

HOW SCIENCE WORKS

Tip: The reaction mechanism is the same for any reaction between an alkene and a halogen. You can use it to predict what the product will be when an alkene you've never seen before reacts with a halogen.

Exam Tip

You could get asked to draw the mechanism for the reaction between any halogen and any alkene — not just bromine and ethene. It's not too hard though — the mechanism is the same for all alkenes, and you'll always end up with a halogen atom added to each of the carbon atoms that were double bonded. Simple as that.

Test for unsaturation

PRACTICAL ACTIVITY GROUP 7

The reaction between alkenes and bromine forms the basis of a test that can be used to distinguish between compounds that contain a double bond (like alkenes) and compounds that don't (like alkanes).

- Use a pipette to add about 2 cm^3 of orange bromine water to a test tube.
- Use a second, clean pipette to add about 2 cm^3 of your unknown hydrocarbon sample to the same test tube.
- Stopper the test tube and give it a quick shake.
- Record any observations in a table of results.

Tip: Make sure you carry out a full risk assessment before you do this experiment in class.

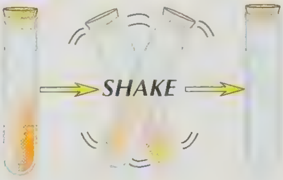


Figure 3: Adding bromine water to a solution containing a carbon-carbon double bond turns the bromine water colourless.

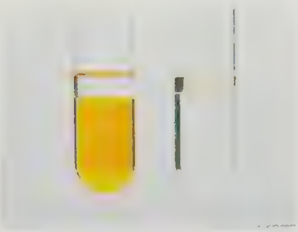


Figure 2: Bromine water has been added to two test tubes. The one on the right contains a compound with a C=C that has decolourised the bromine water. The one on the left contains a substance that doesn't react with bromine.

If your unknown hydrocarbon is an alkene, then when you shake it with bromine water you should see the solution quickly turn from orange to colourless (see Figures 2 and 3). This is because the bromine is added across the double bond to form a colourless dibromoalkane — this happens by electrophilic addition.

Tip: If you don't notice anything happen when you add your hydrocarbon to the bromine water, you should record 'no change' in your table of results as this is still an observation.

Synthesising alcohols

Alkenes can be hydrated by steam at 300 °C and at a pressure of 60-70 atm. The reaction needs a solid phosphoric(V) acid catalyst. The reaction is used industrially to produce ethanol from ethene. Here's the equation for the reaction:

$$H_2C{=}CH_{2(g)} + H_2O_{(g)} \underset{\substack{300\ °C \\ 60\ atm}}{\overset{H_3PO_4}{\rightleftharpoons}} CH_3CH_2OH_{(g)}$$

The reaction's reversible and the reaction yield is low — with ethene it's only about 5%. This sounds rubbish, but you can recycle the unreacted ethene gas, making the overall yield of ethene a much more profitable 95%.

Tip: The reaction between steam and alkenes is also an electrophilic addition reaction. You don't need to worry about the mechanism though — it's a bit different because there's a catalyst involved.

Synthesising haloalkanes

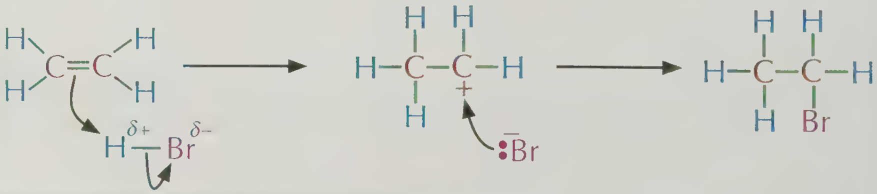
Alkenes undergo electrophilic addition reactions with hydrogen halides to form haloalkanes.

Example

This is the reaction between ethene and hydrogen bromide.

$$H_2C{=}CH_2 + HBr \rightarrow C_2H_5Br$$

It's an electrophilic addition reaction and the mechanism is very similar to the one for the addition of halogens on page 231.



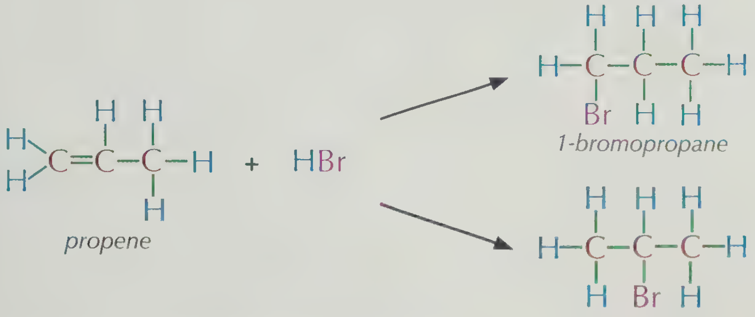
Exam Tip
Other alkenes react in a similar way with HBr. Don't be put off if they give you a different alkene in the exam — the mechanism works in exactly the same way.

Markownikoff's rule

If the hydrogen halide adds to a symmetrical alkene like ethene, only one product can be formed. But if the hydrogen halide adds to an unsymmetrical alkene, there are two possible products.

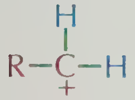
Example

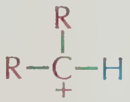
If you add hydrogen bromide to propene, the bromine atom could add to either the first carbon or the second carbon. This means you could produce 1-bromopropane or 2-bromopropane.

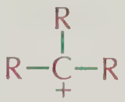


Tip: This electrophilic addition mechanism crops up in loads of different reactions, so make sure you've got it nailed.

The amount of each product formed depends on how stable the carbocation formed in the middle of the reaction is. The three possible carbocations are:


primary carbocation (one R group)

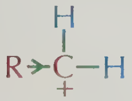

secondary carbocation (two R groups)

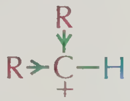

tertiary carbocation (three R groups)

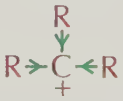
R is an alkyl group — an alkane with a hydrogen removed, e.g. CH_3.

Carbocations with more alkyl groups are more stable because the alkyl groups feed electrons towards the positive charge. You can show that an alkyl group is donating electrons by drawing an arrow on the bond that points to where the electrons are donated.

Tip: The alkyl groups don't give up their electrons to the carbon atom — they just move some of their negatively charged electrons nearer to it, which helps to stabilise the positive charge.


primary carbocation


secondary carbocation


tertiary carbocation

Least stable ⟶ **Most stable**

As a rule, more stable carbocations are much more likely to form than less stable ones. This is because the first step of the mechanism is more likely to lead to the formation of the most stable carbocation. So there will be more of the product formed via the more stable carbocation than there is via the less stable carbocation. This rule can be applied in order to explain what the major product will be when a hydrogen halide reacts with an unsymmetrical alkene.

This can be summed up by Markownikoff's rule, which says that the major product from addition of a hydrogen halide (HX) to an unsymmetrical alkene is the one where hydrogen adds to the carbon with the most hydrogens already attached. The reaction to form this product will have occurred via the most stable carbocation intermediate.

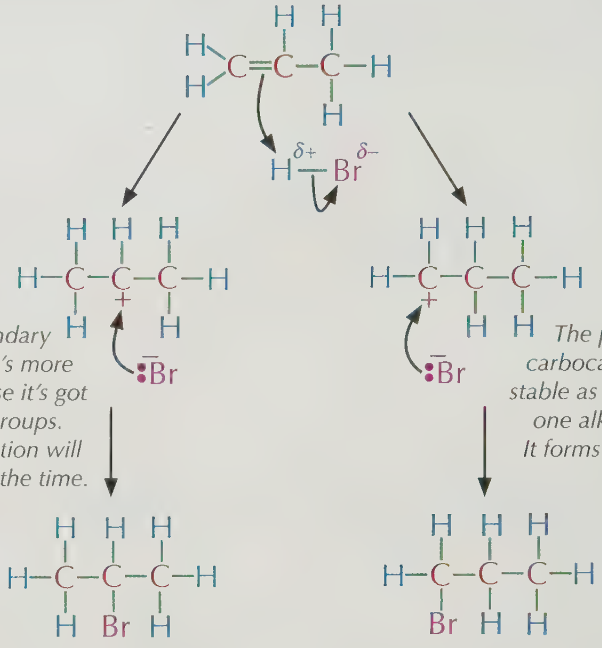
Figure 4: *Vladimir Markownikoff.*

Examples

Here's how hydrogen bromide reacts with propene:

$H_2C{=}CHCH_3 + HBr \rightarrow CH_3CHBrCH_3$
2-bromopropane
major product

$H_2C{=}CHCH_3 + HBr \rightarrow CH_2BrCH_2CH_3$
1-bromopropane
minor product



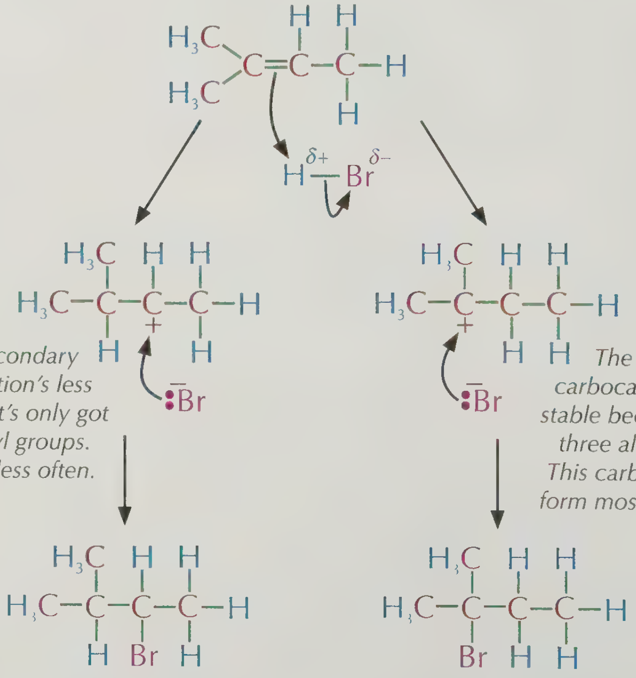
The secondary carbocation's more stable because it's got two alkyl groups. This carbocation will form most of the time.

The primary carbocation's less stable as it's only got one alkyl group. It forms less often.

2-bromopropane major product

1-bromopropane minor product

Here's how hydrogen bromide reacts with 2-methylbut-2-ene:



The secondary carbocation's less stable as it's only got two alkyl groups. It forms less often.

The tertiary carbocation's more stable because it's got three alkyl groups. This carbocation will form most of the time.

2-bromo-3-methylbutane minor product

2-bromo-2-methylbutane major product

Tip: The product that there's most of is called the major product, or the Markownikov product — after the Russian scientist Vladimir Markownikov who came up with the theory that the product formed most often is the one where the hydrogen adds to the carbon atom with the most hydrogen atoms already attached.

Tip: When you're drawing mechanisms make sure the charges balance. That way you'll know if you've managed to lose electrons along the way.

Exam Tip
It makes it easier to see what the main product is if you draw out all the possible cations each time — then there's less chance of making a mistake.

Practice Questions — Application

Q1 Predict the product of the reaction between pent-2-ene and hydrogen gas at 150 °C with a nickel catalyst.

Q2 When propene is added to bromine water, the solution decolourises.

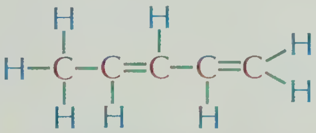
- a) Write an equation for the reaction that is occurring.
- b) Name and outline the mechanism for this reaction.
- c) Bromine water does not decolourise when added to an unknown chemical. What does this tell you about the unknown compound?

Q3 Outline the mechanism for the reaction between but-2-ene and hydrogen bromide.

Q4 a) Draw and name the two different products that could be produced when hydrogen bromide reacts with but-1-ene.

- b) Predict, with reasoning, the major product of the reaction.

Q5 The structure of penta-1,3-diene is shown below:



Draw the products formed when this alkene reacts with HBr.

Tip: Q5 is a bit tricky so here's a hint. If there are two double bonds in an alkene, the addition could occur at either or both of the double bonds, so you'll get more than two products.

Practice Questions — Fact Recall

Q1 What is an electrophile?

Q2 Give two examples of electrophiles.

Q3 What could you react with ethene to produce bromoethane?

Q4 What can you use bromine water to test for?

Q5 Write the equation for the hydration of ethene by steam. Include the conditions for this reaction and the state symbols of all the substances in your answer.

Q6 What does Markownikoff's rule state?

12. Addition Polymers

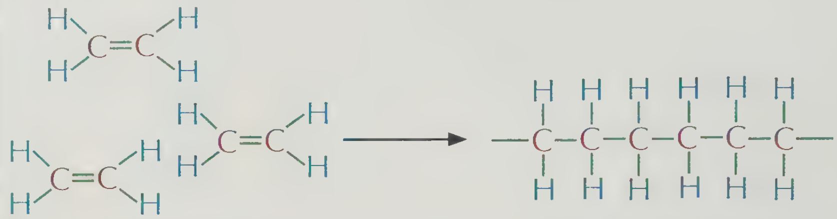
Lots of small molecules (called monomers) can join together to form really long molecules (called polymers). You need to know how alkenes come together to form addition polymers. Read on...

Addition polymers

The double bonds in alkenes can open up and join together to make long chains called **polymers**. It's kind of like they're holding hands in a big line. The individual, small alkenes are called **monomers**. This is called addition polymerisation.

Example

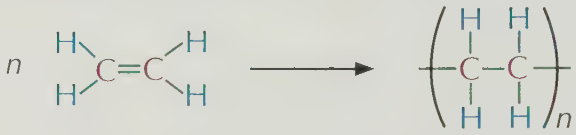
Poly(ethene) is made by the addition polymerisation of ethene.



ethene monomers

a section of poly(ethene)

Addition polymerisation reactions can be written like this...



monomer

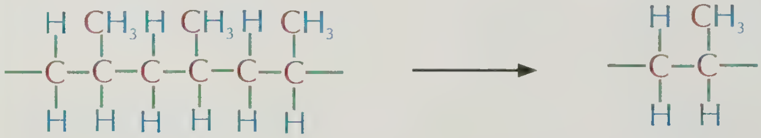
polymer

...where the *n* stands for a very large number of repeat units (monomers) in the polymer — there can be as many as 10 000.

To find the monomer used to form an addition polymer, take the repeat unit and add a double bond.

Example

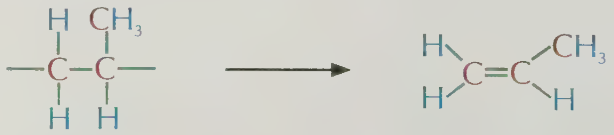
To find the monomer used to make the polymer below you first need to look for the repeat unit.



polymer

repeating unit

Then replace the horizontal carbon-carbon bond with a double bond and remove the unnecessary side bonds to find the monomer.



repeat unit

monomer — propene

Learning Objectives:

- Be able to describe the addition polymerisation of alkenes and substituted alkenes.
- Be able to deduce the repeat unit of an addition polymer from a given monomer.
- Be able to identify the monomer that would produce a given section of an addition polymer.
- Understand the benefits for sustainability of processing waste polymers by combustion for energy production and use as an organic feedstock for the production of plastics and other organic chemicals.
- Understand the need for the removal of toxic waste products, e.g. removal of HCl formed during disposal by combustion of halogenated plastics (e.g. PVC).
- Understand the benefits to the environment of development of biodegradable and photodegradable polymers.

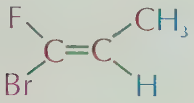
Specification Reference 4.1.3

Tip: The bit inside the brackets is the repeat unit of the polymer. The formula of the polymer is the bit with the brackets and the *n*.

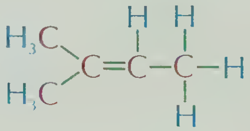
Practice Questions — Application

Q1 Draw the repeating units of the polymers that would be formed from each of these alkenes:

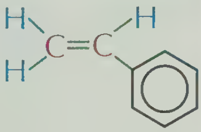
a)



b)

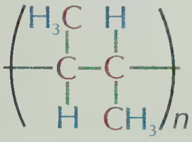


c)

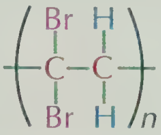


Q2 Draw the alkenes that would form each of these polymers:

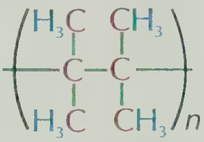
a)



b)



c)



Exam Tip
To pick up the marks in the exam you must show the bonds at the end of the molecule crossing the brackets. This shows that the polymer continues outside the brackets.

Exam Tip
You could be asked to draw 1, 2 or even 3 repeating units in the exam, so make sure you read the question.

The widespread use of polymers

Synthetic polymers have loads of advantages, so they're incredibly widespread these days — we take them pretty much for granted. Just imagine what you'd have to live without if there were no polymers (see Figure 1).

Figure 1: *Some of the many items that are made out of synthetic polymers.*

Exam Tip
If you're asked to name the monomer that forms a particular polymer, draw it out — then you can see what it is and name it using the rules on pages 223-224.

Biodegradability of polymers

One of the really useful things about many everyday polymers is that they're very unreactive. This means food doesn't react with the PTFE coating on pans, plastic windows don't rot, plastic crates can be left out in the rain and they'll be okay, and so on. But this lack of reactivity also leads to a problem. Most polymers aren't biodegradable, and so they're really difficult to dispose of.

Tip: All plastics are made up of polymers

Disposing of waste plastics

In the UK over 2 million tonnes of plastic waste are produced each year. It's important to find ways to get rid of this waste while minimising environmental damage. There are various possible approaches (Figure 2).

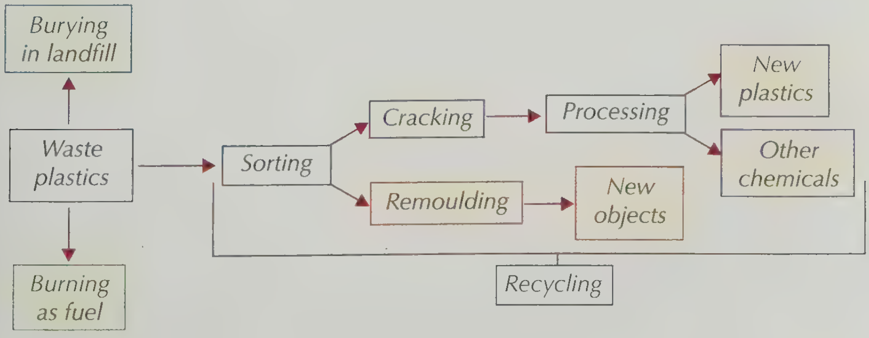


Figure 2: *The different methods for disposing of waste plastic.*

Tip: Plastics are great because they're useful and cheap to make. But they're not so great for the environment if they get thrown away into landfill. So lots of scientific research is going into how we can reuse waste polymers, and how to dispose of them more safely.

HOW SCIENCE WORKS

Burying waste plastic

Landfill is one option for dealing with waste plastics. This means taking waste to a landfill site, compacting it, and then covering it with soil. It is generally used when the plastic is:

- Difficult to separate from other waste.
- Not in sufficient quantities to make separation financially worthwhile.
- Too difficult technically to recycle.

But because the amount of waste we generate is becoming more and more of a problem, there's a need to reduce landfill as much as possible.

Figure 3: *A landfill site — burying waste plastic is one way of disposing of it.*

Tip: See page 4 for more on how society makes decisions about things like recycling and waste plastic.

Recycling plastics

Because many plastics are made from non-renewable oil fractions, it makes sense to recycle plastics as much as possible. There's more than one way to recycle plastics. After sorting into different types, some plastics (poly(propene), for example) can be melted and remoulded, while others can be cracked into monomers which can be used as an organic feedstock to make more plastics or other chemicals.

Burning waste plastic

If recycling isn't possible for whatever reason, waste plastics can be burned — and the heat can be used to generate electricity. This process needs to be carefully controlled to reduce toxic gases. For example, polymers that contain chlorine (such as PVC) produce HCl when they're burned — this has to be removed. Waste gases from the combustion are passed through scrubbers which can neutralise gases such as HCl by allowing them to react with a base.

Making biodegradable polymers

Scientists can now make biodegradable polymers — ones that naturally decompose. Biodegradable polymers decompose pretty quickly in certain conditions — because organisms can digest them.

Biodegradable polymers can be made from materials such as starch (from maize and other plants) and from the hydrocarbon isoprene (2-methyl-1,3-butadiene). So, biodegradable polymers can be produced from renewable raw materials or from oil fractions.

Exam Tip
Weighing up the advantages and disadvantages of things is an important skill in chemistry. You may be asked to do it in your exam, so make sure it's a skill you've mastered.

Advantages of using renewable raw materials

HOW SCIENCE WORKS

Using renewable raw material has several advantages:

- Renewable raw materials aren't going to run out like oil will.
- When polymers biodegrade, carbon dioxide (a greenhouse gas) is produced. If your polymer is plant-based, then the CO_2 released as it decomposes is the same CO_2 absorbed by the plant when it grew. But with an oil-based biodegradable polymer, you're effectively transferring carbon from the oil to the atmosphere.
- Over their 'lifetime' some plant-based polymers save energy compared to oil-based plastics.

But whatever raw material you use, at the moment the energy for making polymers usually comes from fossil fuels.

Tip: Releasing extra CO_2 into the atmosphere adds to the greenhouse effect and warms the Earth. See page 261 for loads more on the greenhouse effect.

Disadvantages of using biodegradable polymers

Although biodegradable polymers sound like a fab idea, there are a few disadvantages of using biodegradable plastics over the standard non-biodegradable ones.

Even though they're biodegradable, these polymers still need the right conditions before they'll decompose. You couldn't necessarily just put them in a landfill and expect them to perish away — because there's a lack of moisture and oxygen under all that compressed soil. You need to chuck them on a big compost heap. This means that you still need to collect and separate the biodegradable polymers from non-biodegradable plastics. At the moment, they're also more expensive than oil-based equivalents.

Figure 4: *A compostable plastic bag.*

Uses of biodegradable polymers

There are various potential uses — e.g. plastic sheeting used to protect plants from the frost can be made from poly(ethene) with starch grains embedded in it. In time the starch is broken down by microorganisms and the remaining poly(ethene) crumbles into dust. There's no need to collect and dispose of the old sheeting.

Other things scientists can do

Developing biodegradable plastics isn't the only thing that chemists can do to decrease the environmental damage caused by waste plastics. Other potential developments to solve the problem include:

- Continuing to develop photodegradable polymers (polymers which can be chemically broken down by light), and introducing them into everyday use.
- Developing better techniques for cracking polymers so that recycling polymers becomes more efficient.
- Finding new ways of making polymers from plant-based substances to reduce the use of finite raw materials like crude oil.
- Using processes with higher atom economy to reduce the amount of waste produced during manufacturing processes.
- Developing new, more efficient ways of sorting and recycling polymers.

Tip: See pages 92-94 for more on atom economy and why high atom economy processes are important.

Practice Questions — Fact Recall

Q1 What types of polymers are formed from alkenes?

Q2 Describe the process that leads to the formation of polymers from alkenes.

Q3 a) Explain why it is good for everyday polymers to be unreactive.

b) What problem does the fact that plastics are unreactive cause?

Q4 Give two ways in which plastics can be recycled.

Q5 Burning plastic produces toxic gases.

a) What toxic gas is produced when poly(chloroethene), also known as PVC, is burnt?

b) How can this toxic gas be removed?

Q6 Give three advantages of making plastic from renewable raw materials rather than non-renewable materials such as oil.

Q7 Suggest two disadvantages of using biodegradable polymers.

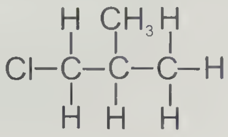
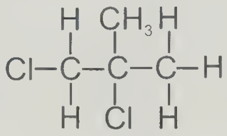
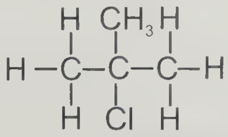
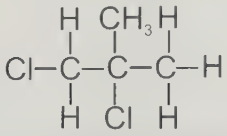
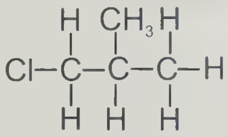
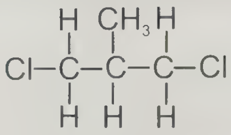
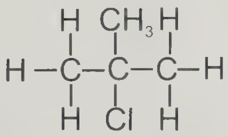
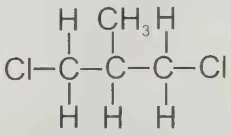
Section Summary

Make sure you know...

- That a functional group is a group of atoms responsible for the characteristic reactions of a compound.
- What general formulas, homologous series, structural formulas, displayed formulas, and skeletal formulas are and how to use them.
- How you can use the general formula of a homologous series to predict the formula of any member of the series.
- What aromatic compounds, aliphatic compounds, alicyclic compounds, alkyl groups, saturated compounds and unsaturated compounds are.
- That structural isomers have the same molecular formula but different structural formulas.
- That alkanes are saturated hydrocarbons that only contain single C–C and C–H bonds.
- How to name alkanes using the IUPAC rules of nomenclature.
- Why atoms form a tetrahedral shape around each carbon atom in alkanes.
- That the single bonds in alkanes are called sigma (σ-) bonds, and they form from the overlap of orbitals directly between the bonding atoms.
- That atoms are free to rotate around sigma bonds.
- That the low reactivity of alkanes is due to the high bond enthalpy and low polarity of the C–C and C–H bonds.
- Why long or linear alkanes have higher boiling points than short or branched alkanes.
- How alkanes may undergo complete or incomplete combustion.
- Why carbon monoxide (CO) is toxic to humans.
- What heterolytic and homolytic fission are.
- That a radical is a species with an unpaired electron, and is represented in mechanisms by a dot next to the species' formula.
- What curly arrows show in reaction mechanisms and how to use them in diagrams.
- How haloalkanes are formed from alkanes in radical substitution reactions.
- The mechanism of radical substitution including initiation, propagation and termination.
- Why you can get a mixture of products in free radical substitution reactions.
- What alkenes are and how to name them.
- The structure of a C=C double bond in terms of pi (π-) and sigma (σ-) bonds.
- How to explain the relatively high reactivity of alkenes due to the low bond enthalpy of the pi bond.
- Why atoms form a trigonal planar shape around each carbon of the C=C double bond of alkenes.
- That stereoisomers have the same structural formula but different arrangements of the atoms in space.
- That *E*/*Z* isomerism and *cis-trans* isomerism are types of stereoisomerism, and why they occur.
- How to use the Cahn-Ingold-Prelog priority rules to identify *E* and *Z* stereoisomers.
- That an electrophile is an electron-pair acceptor.
- The mechanism of electrophilic addition in alkenes and how alkenes react with halogens, halides, steam and hydrogen.
- How to use Markownikoff's rule to predict the formation of a major organic product in addition reactions of H–X to unsymmetrical alkenes.
- How alkenes can join together to form addition polymers.
- How to work out the repeat unit of a polymer given its monomer and how to work out the monomer of a polymer given its repeat unit.
- The benefits for sustainability of processing waste polymers and the potential problems.
- The benefits to the environment of biodegradable and photodegradable polymers.

Exam-style Questions

1 2-methylpropene is an alkene that can react with chlorine or hydrogen chloride in an electrophilic addition reaction. From the table below, choose the correct option which shows the major products for each of these two reactions.

	Reaction with hydrogen chloride	Reaction with chlorine
A	 $\mathrm{ClCH_2CH(CH_3)CH_3}$	 $\mathrm{ClCH_2CCl(CH_3)CH_3}$
B	 $\mathrm{CH_3CCl(CH_3)CH_3}$	 $\mathrm{ClCH_2CCl(CH_3)CH_3}$
C	 $\mathrm{ClCH_2CH(CH_3)CH_3}$	 $\mathrm{ClCH_2CH(CH_3)CH_2Cl}$
D	 $\mathrm{CH_3CCl(CH_3)CH_3}$	 $\mathrm{ClCH_2CH(CH_3)CH_2Cl}$

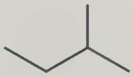
(1 mark)

2 Which of the following options shows the structural formula of methylbutane?

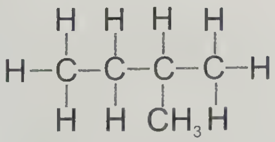
A $\mathrm{CH_3CH(CH_3)CH_2CH_3}$

B $\mathrm{C_5H_{12}}$

C



D



$\mathrm{CH_3CH_2CH(CH_3)CH_3}$

(1 mark)

3 When bromine is exposed to UV light, the Br–Br bond breaks and two radicals are formed.

(a) (i) What are radicals?

(1 mark)

(ii) What name is given to the type of bond fission that produces radicals?

(1 mark)

(b) Bromine reacts with ethane under UV light to form bromoethane.

(i) Write an equation for the formation of bromoethane.

(1 mark)

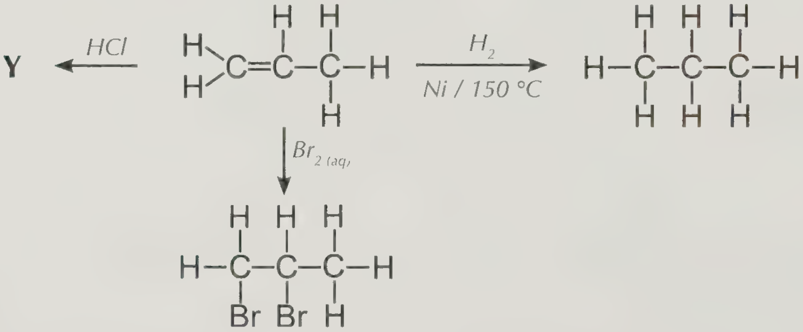
(ii) Outline the mechanism for this reaction, naming each step.

(3 marks)

(c) Suggest two haloalkanes other than bromoethane that could be produced during this reaction.

(2 marks)

4 The scheme below shows some reactions involving propene (C_3H_6):



(a) Alkenes like propene are susceptible to attack by electrophiles.

(i) Draw a diagram to illustrate the structure of a carbon-carbon double bond.

(2 marks)

(ii) Explain why alkenes are susceptible to attack by electrophiles.

(2 marks)

(b) When propene is added to bromine water, 1,2-dibromopropane is produced.

(i) Outline the mechanism for this reaction, including dipoles where relevant.

(4 marks)

(ii) State what you would observe when this reaction takes place.

(1 mark)

(c) When propene reacts with HCl, molecule **Y** is formed.

Suggest two possible structures for molecule **Y**.

(2 marks)

5 2,2,4-trimethylpentane is a branched alkane widely used in petrol.
It is an isomer of the straight-chain alkane octane.

(a) (i) Draw the displayed formula of 2,2,4-trimethylpentane.

(1 mark)

(ii) The boiling point of 2,2,4-trimethylpentane is 372 K. Predict, with reasoning, whether you expect the boiling point of octane to be higher or lower than this.

(4 marks)

(b) Write an equation for the complete combustion of 2,2,4-trimethylpentane.

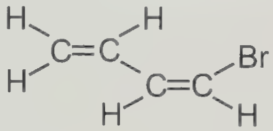
(1 mark)

(c) Alkanes are used as fuel in household appliances. Use your knowledge of combustion to explain the importance of an adequate supply of oxygen to the appliances.

(3 marks)

6 This question is about alkenes and their polymers.

(a) One of the stereoisomers of 1-bromo-1,3-butadiene is shown below:



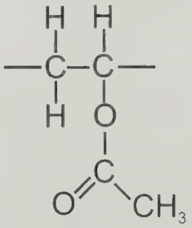
(i) What is stereoisomerism?

(1 mark)

(ii) Draw one other E/Z isomer of 1-bromo-1,3-butadiene and state whether the isomer you have drawn is the E-isomer or the Z-isomer.

(2 marks)

(b) Polyvinylacetate (PVA) is a synthetic polymer. It is one of the main components of PVA glue. The repeating unit of PVA is shown below:



(i) What type of polymer is PVA?

(1 mark)

(ii) Draw the structure of the monomer that gives rise to PVA.

(1 mark)

(c) Alkene-based polymers are extremely useful, but disposing of waste polymers is a big problem. Discuss the advantages and disadvantages of using biodegradable polymers.

(4 marks)

Module 4 Section 2: Alcohols and Haloalkanes

1. Properties of Alcohols

Learning Objectives:

- Be able to use the IUPAC rules of nomenclature to systematically name alcohols.
- Be able to classify alcohols as primary, secondary and tertiary alcohols.
- Be able to explain the polarity of alcohols.
- Be able to explain, in terms of hydrogen bonding, the water solubility and the relatively low volatility of alcohols compared with alkanes.

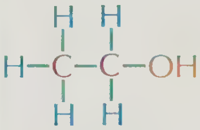
Specification Reference
4.1.1, 4.2.1

Alcohols are organic compounds that contain an -OH functional group. This dramatically affects their physical properties compared to alkanes. Before you get on to that though, you need to know how to name them.

Nomenclature of alcohols

The **alcohol** homologous series has the general formula $C_nH_{2n+1}OH$. Alcohols are named using the same IUPAC naming rules as alkanes (see pages 211-213), but the suffix -ol is added in place of the -e on the end of the name.
You also need to indicate which carbon atom the alcohol functional group is attached to — the carbon number(s) comes before the -ol suffix.
If there are two -OH (hydroxyl) groups the molecule is a -diol, and if there are three it's a -triol.

Examples



ethanol

The molecule is a saturated hydrocarbon where the longest continuous carbon chain is 2 carbon atoms, so the stem is eth- and the name will be based on 'ethane'.

There's one -OH attached to the carbon chain, so the suffix is -ol.

No matter which carbon atom the -OH group is attached to, the molecule will be exactly the same (-OH will always be attached to carbon atom 1), so there's no need to put a number.

So, the alcohol is called ethanol.

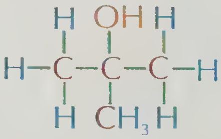
The molecule is a saturated hydrocarbon where the longest continuous carbon chain is 3 carbon atoms, so the stem is prop- and the name will be based on 'propane'.

There's one -OH attached to the carbon chain, so the suffix is -ol.

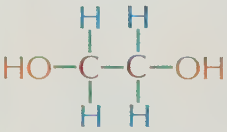
It's attached to the second carbon, so there's a 2 before the -ol.

There's also a methyl group attached to the second carbon, so there's a 2-methyl- prefix.

The alcohol is called 2-methylpropan-2-ol.



2-methylpropan-2-ol



ethane-1,2-diol

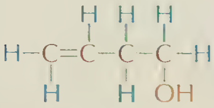
The molecule is a saturated hydrocarbon where the longest continuous carbon chain is 2 carbon atoms, so the stem is eth- and the name will be based on 'ethane'.

There are two -OH groups attached to the carbon chain, so the suffix is -diol.

There's one -OH attached to each carbon atom, so there's a 1,2- before the -diol.

So, the alcohol is called ethane-1,2-diol.

Tip: It's pretty easy naming alcohols with saturated carbon chains. But if an alcohol is unsaturated (i.e. contains an alkene group), you need to remember to include it in the name too. E.g.:



This molecule has a name based on 'butene' — it's 3-buten-1-ol.

Tip: If the alcohol functional group (-OH) is the most important one then the name ends in -ol, like in these examples. Otherwise, the molecule gets a hydroxy- prefix instead. For example, 1-hydroxypropanone.

Primary, secondary and tertiary alcohols

An alcohol can be primary, secondary or tertiary, depending on which carbon atom the hydroxyl group -OH is bonded to. Primary alcohols are given the notation 1° and the -OH group is attached to a carbon with one alkyl group attached. Secondary alcohols are given the notation 2° and the -OH group is attached to a carbon with two alkyl groups attached. Tertiary alcohols are given the notation 3° (you can see where I'm going with this) and the -OH group is attached to a carbon with three alkyl groups attached (see Figure 1).

Tip: Remember that an alkyl group is an alkane with a hydrogen removed, for example CH_3 or CH_3CH_2.

Tip: 'R' just means any alkyl group.

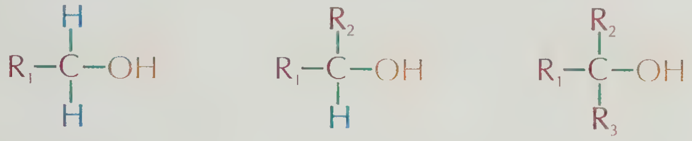
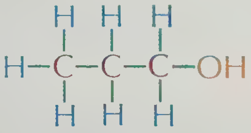

primary alcohol *secondary alcohol* *tertiary alcohol*

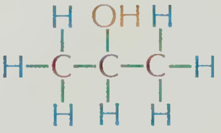
Figure 1: *Diagrams of 1°, 2° and 3° alcohols.*

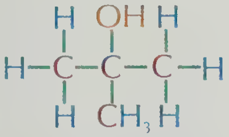
Examples


propan-1-ol

Propan-1-ol is a primary (1°) alcohol because the carbon the -OH group is attached to is attached to one alkyl group (CH_3CH_2).

Propan-2-ol is a secondary (2°) alcohol because the carbon the -OH group is attached to is attached to two alkyl groups (CH_3 and CH_3).


propan-2-ol


2-methylpropan-2-ol

2-methylpropan-2-ol is a tertiary (3°) alcohol because the carbon the -OH group is attached to is attached to three alkyl groups (CH_3, CH_3 and CH_3).

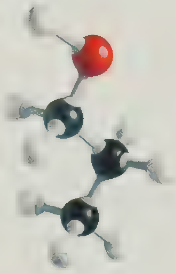


Figure 2: *A molecular model of propan-1-ol.*

Tip: Alcohols can react in different ways depending on whether they are primary, secondary or tertiary — so it's important that you know the difference between them.

Physical properties of alcohols

Alcohols are generally polar molecules due to the electronegative hydroxyl group which pulls the electrons in the C–OH bond away from the carbon atom. The hydroxyl group (-OH) is also polar, with a δ– charge on the oxygen atom and a δ+ charge on the hydrogen atom (see Figure 3).

$$\overset{\delta+}{R_1}-\overset{\delta-}{O}-\overset{\delta+}{H}$$

Figure 3: *Charge distribution in an alcohol.*

Tip: Electronegativity is the ability of an atom to attract the bonding electrons in a covalent bond. There's more about it on page 120.

The partial positive charge on the hydrogen atom in the hydroxyl group can attract the lone pairs on an oxygen from a neighbouring molecule, forming **hydrogen bonds**. This gives alcohols certain properties...

When you mix an alcohol with water, hydrogen bonds form between the -OH group and H_2O — see Figure 4.

Exam Tip
If you're asked to draw hydrogen bonding in an exam don't forget to mark on the lone pairs of electrons and label the hydrogen bond and all the δ+ and δ– atoms.

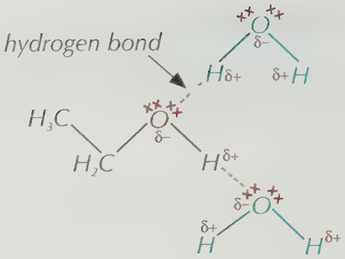


Figure 4: *Hydrogen bonding of ethanol in water.*

If it's a small alcohol (e.g. methanol, ethanol or propan-1-ol), hydrogen bonding lets it mix freely with water — it's soluble in water. In larger alcohols, most of the molecule is a non-polar carbon chain, so there's less attraction for the polar H_2O molecules. This means that as alcohols increase in size, their solubility in water decreases.

Alcohols also form hydrogen bonds with each other. Hydrogen bonding is the strongest kind of intermolecular force, so it gives alcohols a relatively low volatility (they don't evaporate easily into a gas) and relatively high boiling points compared to non-polar compounds of similar sizes, e.g. alkanes.

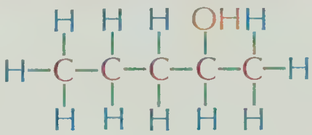
Tip: The volatility of a substance is its tendency to evaporate (turn into a gas).

Tip: Their relatively high boiling points mean that alcohols are liquids at room temperature.

Practice Questions — Application

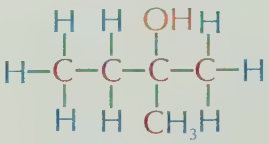
Q1 Name the following alcohols.

a)



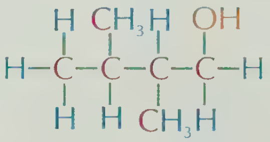
$$H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{OH}{C}}-\underset{H}{\overset{H}{C}}-H$$

b)



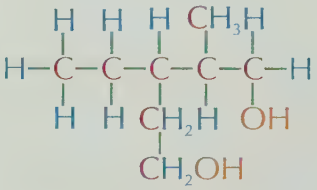
$$H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{CH_3}{\overset{OH}{C}}-\underset{H}{\overset{H}{C}}-H$$

c)



$$H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{CH_3}{C}}-\underset{CH_3}{\overset{H}{C}}-\underset{H}{\overset{OH}{C}}-H$$

d)



$$H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{\underset{CH_2OH}{CH_2}}{\overset{H}{C}}-\underset{H}{\overset{CH_3}{C}}-\underset{OH}{\overset{H}{C}}-H$$

Tip: Remember — name molecules so that the names include the lowest numbers possible.

Tip: When you're naming diols, the stem of the name must come from the longest carbon chain that includes both hydroxy groups.

Q2 State whether each of the alcohols in Question 1, parts a), b) and c), are primary (1°), secondary (2°) or tertiary (3°) alcohols.

Q3 Which alcohol is more soluble in water:
propan-1-ol or octan-1-ol? Explain your answer.

Q4 Which of these molecules will have a higher boiling point:
butane or butan-1-ol? Explain your answer.

Tip: When you're naming diols, you keep the 'e' at the end of the alkane name. You lose it when naming alcohols with only one -OH group. For example:
- butanol (not butaneol),
- hexanediol (not hexandiol).

Practice Questions — Fact Recall

Q1 What suffix is added to a molecule's name if an -OH functional group is the highest priority group in the molecule?

Q2 What is a secondary alcohol?

Q3 Draw a diagram to show the hydrogen bonding present between a molecule of ethanol and water.

2. Reactions of Alcohols

Alcohols can react in a number of different ways. In substitution reactions, the hydroxyl group is replaced by a different functional group, and in elimination reactions the alcohol loses a molecule of water to form an alkene.

Substitution reactions of alcohols

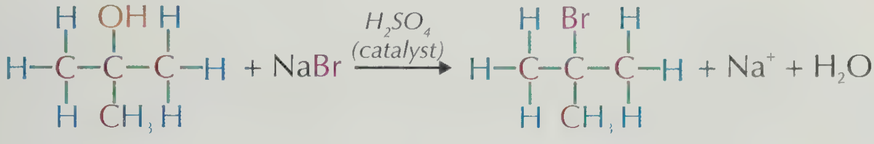
Alcohols will react with compounds containing halide ions (such as NaBr) in a **substitution reaction**. The hydroxyl (-OH) group is replaced by the halide, so the alcohol is transformed into a **haloalkane**. The reaction also requires an acid catalyst, such as H_2SO_4. A general reaction is shown in Figure 1.

$$\underset{\text{alcohol}}{R-OH} + NaX \xrightarrow{H^+\text{ (catalyst)}} \underset{\text{haloalkane}}{R-X} + Na^+ + H_2O$$

Figure 1: *The general equation for the reaction of a sodium halide with an alcohol.*

Example

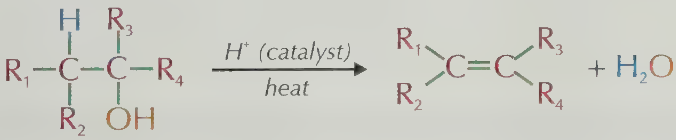
To make 2-bromo-2-methylpropane you just need to shake 2-methylpropan-2-ol (a tertiary alcohol) with sodium bromide and concentrated sulfuric acid at room temperature.



2-methylpropan-2-ol *2-bromo-2-methylpropane*

Elimination reactions of alcohols

Alkenes are really useful organic chemicals that can be used as starting products for lots of organic chemicals such as polymers (see pages 236-239). You can make alkenes by eliminating water from alcohols in an **elimination reaction**. The alcohol is mixed with an acid catalyst — either concentrated sulfuric acid (H_2SO_4) or concentrated phosphoric acid (H_3PO_4). The mixture is then heated. Water is eliminated from the alcohol, so this reaction is sometimes called a dehydration reaction. The general reaction for the dehydration of alcohols is shown in Figure 2.

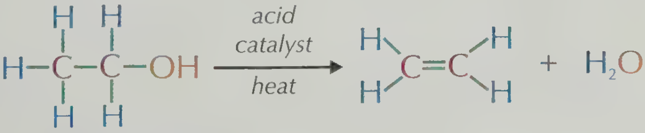


alcohol *alkene*

Figure 2: *The general equation for the dehydration of an alcohol to form an alkene.*

Example

You can make ethene by eliminating water from ethanol in a dehydration reaction. The ethanol is mixed with an acid catalyst and heated to 170 °C.



ethanol *ethene*

Learning Objectives:

- Know that alcohols undergo substitution reactions with halide ions in the presence of acid (e.g. $NaBr/H_2SO_4$) to form haloalkanes.
- Know that H_2O can be eliminated from alcohols in the presence of an acid catalyst (e.g. H_3PO_4 or H_2SO_4) and heat to form alkenes.

Specification Reference 4.2.1

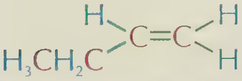
Tip: 'X' just represents any halogen, for example Cl or Br.

Tip: Catalysts speed up a reaction without being used up themselves (see page 182). In the acid-catalysed substitution of alcohols by halide compounds, the water that forms can dissociate to form H^+ and OH^- ions, so the H^+ ions that catalyse the reaction are regenerated.

Tip: In a dehydration reaction water is lost from one of the reactants. It's the opposite of the hydration reaction on page 232.

The water molecule that is eliminated from an alcohol when it forms an alkene is made up from the hydroxyl group and a hydrogen atom that was bonded to a carbon atom adjacent to the hydroxyl carbon. This means that often there are two possible alkene products from one elimination reaction depending on which side of the hydroxyl group the hydrogen is eliminated from. Sometimes an alkene product can form *E/Z* isomers (see page 227) — if this is the case then a mixture of both isomers will form.

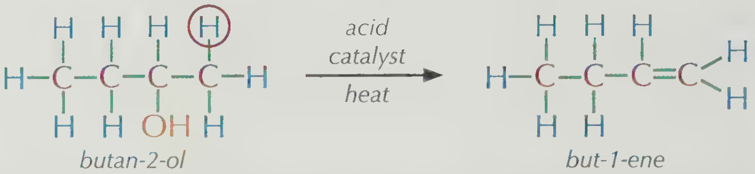
Tip: But-1-ene doesn't form *E/Z* isomers because there are two identical (hydrogen) groups attached to one of the C=C carbons:



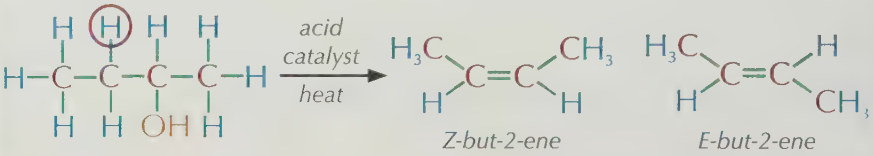
Example

When butan-2-ol is heated with concentrated phosphoric acid, elimination can occur between the hydroxyl group and the hydrogen either on carbon-1 or carbon-3. This results in the formation of a mixture of alkene products — but-1-ene, *E*-but-2-ene and *Z*-but-2-ene.

- Elimination between the hydroxyl group and a hydrogen on carbon-1 results in the formation of but-1-ene.



- Elimination between the hydroxyl group and a hydrogen on carbon-3 results in the formation of but-2-ene. Since but-2-ene is able to form *E/Z* isomers, a mixture of *E*-but-2-ene and *Z*-but-2-ene will form.



Tip: The mixture of *E* and *Z* isomers doesn't have to be an equal ratio — often you'll end up with more of one isomer than the other.

Practice Questions — Application

Q1 2-chloro-2-methyl-propane can be synthesised from an alcohol in a one-step reaction.
Give the reagents and conditions needed for this reaction.

Q2 Draw and name all the organic products formed when 4-methyl-hexan-3-ol is heated with concentrated phosphoric acid.

Tip: You may need to have a look back at pages 223-224 for the IUPAC rules on naming alkenes.

Practice Questions — Fact Recall

Q1 a) Write the equation for the general reaction between an alcohol and a sodium halide.

b) What type of reaction is this?

Q2 a) Write down the equation for the dehydration of ethanol.

b) Name the products of this reaction.

c) Name a catalyst that could be used to catalyse this reaction.

Q3 Explain why the elimination reaction of an alcohol can result in the formation of a mixture of organic products.

3. Oxidising Alcohols

You can oxidise alcohols by burning them. But that's not all. You can also oxidise primary and secondary alcohols with certain oxidising agents to create molecules containing a carbon-oxygen double bond. Substances that contain these carbon-oxygen double bonds are known as carbonyl compounds.

Combustion of alcohols

The simple way to oxidise alcohols is to burn them. It doesn't take much to set ethanol alight and it burns with a pale blue flame. The C–C and C–H bonds are broken as the ethanol is completely oxidised to make carbon dioxide and water. This is a **combustion** reaction (see page 217).

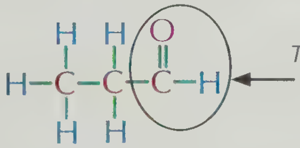
$$C_2H_5OH_{(l)} + 3O_{2(g)} \rightarrow 2CO_{2(g)} + 3H_2O_{(g)}$$

But if you want to end up with something more interesting, you need a more sophisticated way of oxidising. You can use the oxidising agent acidified potassium dichromate(VI) ($K_2Cr_2O_7/H_2SO_4$) to mildly oxidise alcohols.

Primary alcohols are oxidised to **aldehydes** and then to **carboxylic acids**. Secondary alcohols are oxidised to **ketones** only. In these reactions, the orange dichromate(VI) ion, $Cr_2O_7^{2-}$, is reduced to the green chromium(III) ion, Cr^{3+}. Tertiary alcohols won't be oxidised, so a solution containing dichromate(VI) ions and a tertiary alcohol will stay orange. These colour changes can be used as a test to distinguish tertiary alcohols from primary and secondary alcohols (see page 252).

Aldehydes, ketones and carboxylic acids

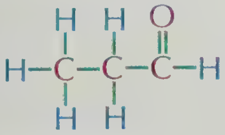
Aldehydes and ketones are carbonyl compounds — they have the functional group C=O. Their general formula is $C_nH_{2n}O$. Aldehydes have a hydrogen and one alkyl group attached to the **carbonyl** carbon atom...



This is the aldehyde functional group.

Aldehydes have the suffix -al. You don't have to say which carbon the functional group is on — it's always on carbon-1. Naming aldehydes follows very similar rules to the naming of alcohols (see page 244).

Examples



propanal

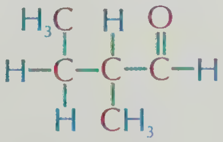
The molecule has a saturated carbon skeleton, and the longest continuous carbon chain is 3 carbon atoms, so the stem is prop- and the name is based on 'propane'.

So, the aldehyde is called propanal.

The molecule has a saturated carbon skeleton, and the longest continuous carbon chain is 4 carbon atoms, so the stem is butane.

There's a methyl group attached to the second carbon atom, so there's a 2-methyl- prefix.

So, the aldehyde is called 2-methylbutanal.



2-methylbutanal

Learning Objectives:

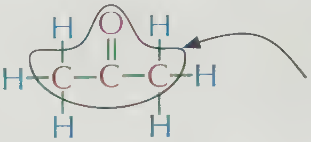
- Be able to describe the combustion of alcohols.
- Be able to use the IUPAC rules of nomenclature to systematically name aldehydes, ketones and carboxylic acids.
- Know that you can oxidise alcohols using an oxidising agent, such as $Cr_2O_7^{2-}/H^+$ (i.e. $K_2Cr_2O_7/H_2SO_4$).
- Be able to describe the oxidation of primary alcohols to form aldehydes and carboxylic acids.
- Be able to describe how you can control the oxidation product of a primary alcohol using different reaction conditions.
- Be able to describe the oxidation of secondary alcohols to form ketones.
- Know that tertiary alcohols are resistant to oxidation.
- Be able to carry out qualitative tests to distinguish tertiary alcohols from primary and secondary alcohols (PAG 7).

Specification Reference 4.1.1, 4.2.1

Tip: Remember that a suffix comes at the end of a name and a prefix comes at the beginning.

Tip: A molecule has to contain at least 3 carbon atoms for it to be a ketone.

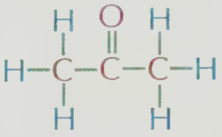
Ketones have two alkyl groups attached to the carbonyl carbon atom.



This is the ketone functional group.

The suffix for ketones is -one. For ketones with five or more carbons, you always have to say which carbon the functional group is on. (If there are other groups attached, such as methyl groups, you have to say what carbon the ketone group is on for ketones with a stem of four or more carbons too.)

Examples



propanone

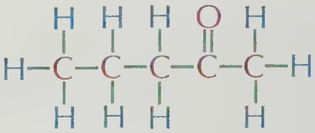
The molecule has a saturated carbon skeleton and the longest continuous carbon chain is 3 carbon atoms, so the stem is prop- and the name is based on 'propane'.

So, the ketone is called propanone.

The molecule has a saturated carbon skeleton and the longest continuous carbon chain is 5 carbon atoms, so the stem is pent- and the name is based on 'pentane'.

The carbonyl is found on the second carbon atom.

So, the ketone is called pentan-2-one.

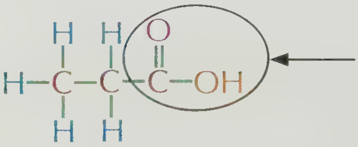


pentan-2-one

Figure 1: *The ketone propanone (also known as acetone) is commonly used as a nail varnish remover.*

Tip: The carboxylic acid functional group is written as COOH and not CO_2H to show that the two oxygens are different — one is part of a carbonyl group (CO) and the other is part of an OH group.
The same idea applies to aldehydes — you always write the functional group out as CHO (not COH) so it doesn't look like an alcohol.

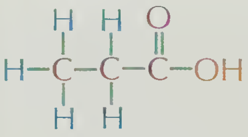
Carboxylic acids have a COOH group at the end of their carbon chain.



This is the carboxylic acid functional group.

The suffix for carboxylic acids is -oic, and you also add the word 'acid' to the end of the name.

Examples



propanoic acid

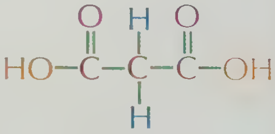
The carbon skeleton is saturated and the longest continuous carbon chain is 3 carbon atoms, so the stem is prop- and the name is based on 'propane'.

So, the carboxylic acid is called propanoic acid.

The carbon skeleton is saturated and the longest continuous carbon chain is 3 carbon atoms, so the stem is prop- and the name is based on 'propane'.

There's a COOH group at each end of the carbon chain so it has a -dioic acid suffix.

So, the carboxylic acid is called propanedioic acid.

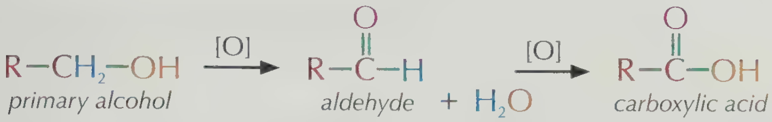


propanedioic acid

Tip: As with diols, dicarboxylic acids keep the 'e' at the end of the alkane stem.
So the example on the right is propanedioic acid, and not propandioic acid.

Oxidation of primary alcohols

A primary alcohol is first oxidised to an aldehyde. This aldehyde can then be oxidised to a carboxylic acid. You can use the notation [O] to represent an oxidising agent — this saves you having to write down acidified potassium dichromate(VI) every time you write out a reaction, which is handy. This means you can write equations like this:

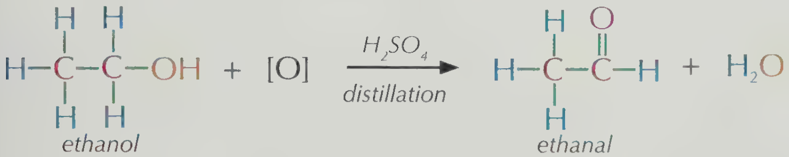


$$\mathrm{R{-}CH_2{-}OH} \xrightarrow{[O]} \mathrm{R{-}\overset{O}{\overset{\|}{C}}{-}H} + \mathrm{H_2O} \xrightarrow{[O]} \mathrm{R{-}\overset{O}{\overset{\|}{C}}{-}OH}$$

You can control how far the alcohol is oxidised by controlling the reaction conditions.

Oxidising primary alcohols to aldehydes

Gently heating ethanol with potassium dichromate(VI) solution and sulfuric acid in a test tube should produce "apple" smelling ethanal (an aldehyde).

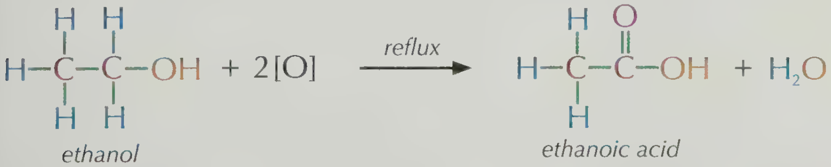


$$\mathrm{H{-}\underset{H}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}{-}OH} + [O] \xrightarrow[\text{distillation}]{H_2SO_4} \mathrm{H{-}\underset{H}{\overset{H}{C}}{-}\overset{O}{\overset{\|}{C}}{-}H} + \mathrm{H_2O}$$

However, it's really tricky to control the amount of heat and the aldehyde is usually oxidised to form "vinegar" smelling ethanoic acid. To get just the aldehyde, you need to get it out of the oxidising solution as soon as it's formed. You can do this by gently heating excess alcohol with a controlled amount of oxidising agent in a distillation apparatus (see Figure 2), so the aldehyde (which boils at a lower temperature than the alcohol) is distilled off immediately.

Oxidising primary alcohols to carboxylic acids

To produce the carboxylic acid, the alcohol has to be vigorously oxidised.

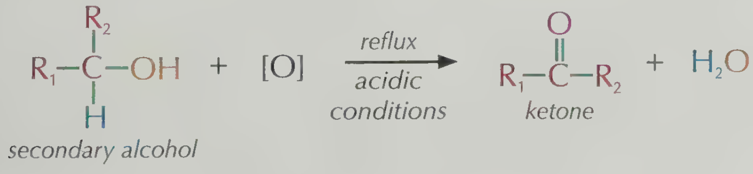


$$\mathrm{H{-}\underset{H}{\overset{H}{C}}{-}\underset{H}{\overset{H}{C}}{-}OH} + 2[O] \xrightarrow{\text{reflux}} \mathrm{H{-}\underset{H}{\overset{H}{C}}{-}\overset{O}{\overset{\|}{C}}{-}OH} + \mathrm{H_2O}$$

The alcohol is mixed with excess oxidising agent and heated under **reflux** (see Figure 3). Heating under reflux means you can increase the temperature of an organic reaction to boiling without losing volatile solvents, reactants or products. Any vaporised compounds are cooled, condense and drip back into the reaction mixture.

Oxidation of secondary alcohols

Refluxing a secondary alcohol with acidified dichromate(VI) will produce a ketone.



$$\mathrm{R_1{-}\underset{H}{\overset{R_2}{C}}{-}OH} + [O] \xrightarrow[\text{acidic conditions}]{\text{reflux}} \mathrm{R_1{-}\overset{O}{\overset{\|}{C}}{-}R_2} + \mathrm{H_2O}$$

Exam Tip
Make sure you learn the conditions required to produce aldehydes and carboxylic acids — it can be pretty easy to mix them up.

Tip: Make sure you balance the oxidising agents when you're writing these equations.

Tip: There's loads more about distillation, reflux and other organic techniques on pages 279-281.

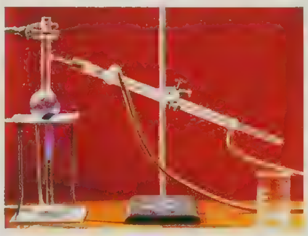


Figure 2: *Distillation apparatus.*

Tip: Heating the alcohol under reflux means that, although you still make an aldehyde first, it stays in the reaction vessel with the oxidising agent — so it oxidises further to give a carboxylic acid.

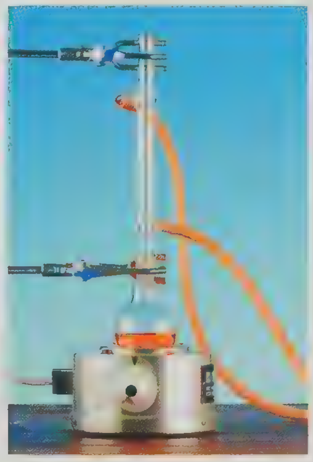
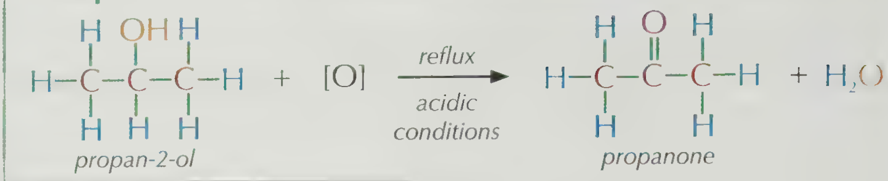


Figure 3: *Reflux apparatus.*

Exam Tip
You might get a more complicated molecule than this in the exam, but just remember — if it's a primary or secondary alcohol and you treat it with acidified potassium dichromate, the hydroxyl groups will turn into carbonyl groups.

Example



Ketones can't be oxidised easily, so even prolonged refluxing won't produce anything more.

Oxidation of tertiary alcohols

Tertiary alcohols don't react with acidified potassium dichromate(VI) at all — the solution stays orange. The only way to oxidise tertiary alcohols is by burning them.

PRACTICAL ACTIVITY GROUP 7

You can use the resistance of tertiary alcohols to oxidation to distinguish them from primary and secondary alcohols. If you heat a sample of an unknown alcohol in a test tube with a few drops of orange potassium dichromate(VI) and a few drops of concentrated sulfuric acid then the solution will stay orange if the alcohol is a tertiary alcohol because they can't be oxidised. If it's a secondary or a primary alcohol the solution will turn green as the alcohol is oxidised and the orange dichromate(VI) ions are reduced to green chromium(III) ions (see Figures 4a and 4b).

Tip: Always carry out a full risk assessment and take appropriate safety precautions when carrying out any experiments.

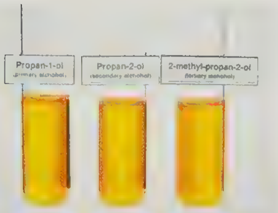

Propan-1-ol (primary alcohol)
Propan-2-ol (secondary alcohol)
2-methyl-propan-2-ol (tertiary alcohol)

Figure 4a: *A primary alcohol (left), a secondary alcohol (middle) and a tertiary alcohol (right) at the start of a reaction with acidified potassium dichromate(VI).*

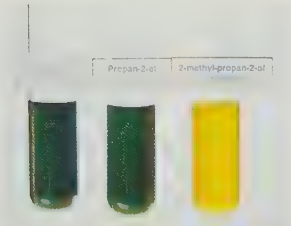
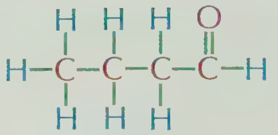


Figure 4b: *Primary (left) and secondary (middle) alcohols are oxidised, causing a colour change from orange to green as Cr(VI) is reduced to Cr(III). Tertiary alcohols are resistant to oxidation, so no colour change is seen (right).*

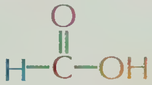
Practice Questions — Application

Q1 Name the following molecules:

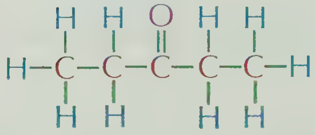
a)



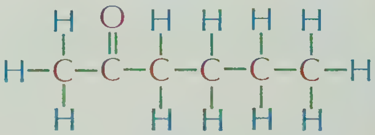
b)



c)



d)



Q2 Draw the structures of the organic products of the following reactions.

a) A reaction between butan-2-ol and acidified potassium dichromate(VI) under reflux.

b) A reaction between butan-1-ol and acidified potassium dichromate(VI) using distillation apparatus.

c) A reaction between butan-1-ol and acidified potassium dichromate(VI) under reflux.

Practice Questions — Fact Recall

Q1 Write an equation for the complete combustion of ethanol.

Q2 Give the functional groups of the following compounds:

a) aldehydes b) ketones c) carboxylic acids

Q3 Write a general equation for the reaction of a primary alcohol with an oxidising agent under reflux.

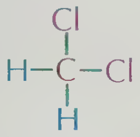
4. Haloalkanes

Haloalkanes pop up a lot in chemistry, so it's important that you know exactly what they are and how they behave. You'll meet a fair few reactions and mechanisms over the next few pages, but they're all pretty similar so you don't need to fret too much about it.

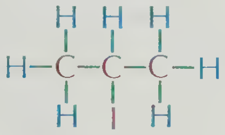
What are haloalkanes?

A **haloalkane** is an alkane with at least one halogen atom in place of a hydrogen atom.

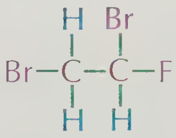
Examples



dichloromethane



2-iodopropane



1,2-dibromo-1-fluoroethane

Naming haloalkanes

You name haloalkanes in exactly the same way that alkanes are named (see pages 211-213), but you have to add a prefix before the name of the alkane (see Figure 1). The prefixes are always placed in alphabetical order. If you have multiple halogens of the same type within a molecule, you use the prefixes di- (for two) or tri- (for three), as you have done when naming other organic compounds. These prefixes don't affect the order that you write the halogens in. For example, trichloro- would still be written before iodo-.

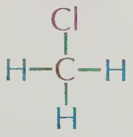
Halogen	Prefix
Fluorine	*fluoro-*
Chlorine	*chloro-*
Bromine	*bromo-*
Iodine	*iodo-*

Figure 1: *Prefixes for naming haloalkanes.*

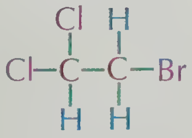
Examples

The molecule is saturated and the longest carbon chain is 1 carbon atom, so the stem is meth- and the name is based on methane.

There's one chlorine atom attached to the carbon atom, so it has a chloro- prefix: chloromethane.



chloromethane



2-bromo-1,1-dichloroethane

The molecule is saturated and the longest carbon chain is 2 carbon atoms, so the stem is eth- and the name is based on ethane.

There's one bromine atom attached to the second carbon atom, so it has a bromo- prefix.

There are two chlorine atoms attached to the first carbon, so it also has the prefix dichloro-.

So the molecule is 2-bromo-1,1-dichloroethane.

Learning Objectives:

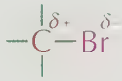
- Be able to apply IUPAC rules of nomenclature to systematically name haloalkanes.
- Be able to define and use the definition of the term nucleophile (an electron pair donor).
- Know that haloalkanes can be hydrolysed in substitution reactions by aqueous alkali and by water.
- Understand the mechanism of nucleophilic substitution in the hydrolysis of primary haloalkanes with aqueous alkali.
- Be able to explain the trend in the rates of hydrolysis of primary haloalkanes in terms of the bond enthalpies of carbon–halogen bonds.
- Know that the hydrolysis of haloalkanes by water in the presence of $AgNO_3$ and ethanol can be used to compare experimentally the rates of hydrolysis of different carbon-halogen bonds.
- Be able to carry out qualitative tests to identify the halogen present in a haloalkane (PAG 7).

Specification Reference
4.1.1, 4.2.2

Polarity of haloalkanes

Halogens are generally much more electronegative than carbon, so the carbon-halogen bond is **polar**.

Example



The bromine atom is more electronegative than the carbon atom and so withdraws electron density from the carbon-bromine bond. This leaves the carbon atom with a partial positive charge and the bromine atom with a partial negative charge.

The δ+ carbon is electron deficient (it doesn't have enough electrons). This means it can be attacked by a **nucleophile**. A nucleophile's an electron-pair donor. It donates an electron pair to somewhere without enough electrons.

Tip: Nucleophiles are often negative ions which, because they form by gaining electrons, have extra electrons that they can donate. Nucleophiles don't have to be ions though. For example, NH_3 is a nucleophile — it's got a non-bonding pair of electrons that it can donate.

Examples

Here are some nucleophiles that will react with haloalkanes.

$:\overline{C}N$	$:NH_3$	$:\overline{O}H$
cyanide ion	*ammonia*	*hydroxide ion*

The pairs of dots represent lone pairs of electrons.
Water's a nucleophile too, but it reacts slowly.

There are examples of reactions where nucleophiles react with haloalkanes on the next few pages.

Exam Tip
If you're asked to outline a mechanism using a nucleophile that you're not familiar with — don't panic. Just follow this general mechanism and you'll be fine.

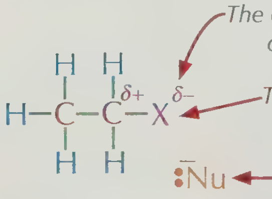
Nucleophilic substitution reactions

Mechanisms are step-by-step sequences of how reactions work. They're often shown as diagrams. They show how the bonds in molecules are made and broken, how the electrons are transferred and how you get from the reactants to the products. Haloalkanes react in **nucleophilic substitution reactions**. In a nucleophilic substitution reaction, a nucleophile attacks a polar molecule, kicks out a functional group and settles itself down in its place. The general equation for a nucleophilic substitution reaction of a haloalkane is:

$$RX + Nu^- \rightarrow RNu + X^-$$

HOW SCIENCE WORKS

The reaction mechanism explains how and why haloalkanes will react this way:



The carbon-halogen bond is polar. The tiny charges on the atoms are shown by δ+ and δ– signs.

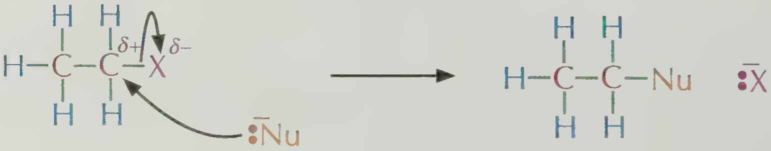
The X stands for one of the halogens (F, Cl, Br or I).

:Nu⁻ stands for a nucleophile (e.g. :OH⁻). The ':' represents the lone pair of electrons and the '–' shows that it has a negative charge.

Tip: If the nucleophile isn't charged, don't just go ahead and write a negative charge. It will just be :Nu (e.g. $:NH_3$).

Tip: In mechanism diagrams, curly arrows always show the movement of an electron pair (see page 220).

The lone pair of electrons on the nucleophile attacks the slightly positive charge on the carbon to create a new bond. This is shown by a curly arrow.



Tip: The bond breaking between the carbon atom and the halogen atom is heterolytic bond breaking — both of the bonding electrons are taken by the halogen.

The carbon can only be bonded to four other atoms so the addition of the nucleophile breaks the bond between the carbon and the halogen — this is shown by another curly arrow. The pair of electrons from the carbon-halogen bond are taken by the halogen and become a lone pair.

Hydrolysis of haloalkanes

In **hydrolysis** reactions, molecules are split up by water molecules (which also split apart). Haloalkanes can be hydrolysed to make alcohols. There's a couple of ways of doing this.

1. Hydrolysis with aqueous alkali

Haloalkanes are hydrolysed by warm aqueous alkali, such as sodium hydroxide (NaOH) solution or potassium hydroxide (KOH) solution, in a nucleophilic substitution reaction. The general equation for this reaction is:

$$RX + {}^{-}OH \rightarrow ROH + X^{-}$$

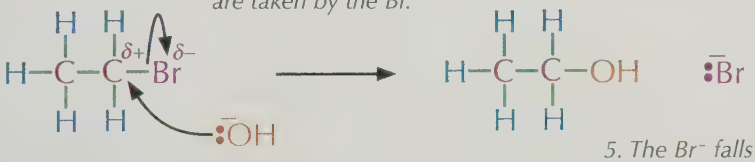
R represents an alkyl group. X stands for one of the halogens (Cl, Br or I). As it's a nucleophilic substitution reaction, the nucleophile (${}^{-}OH$) kicks out the halogen (X) from the RX molecule and takes its place.

Example

Bromoethane can be hydrolysed to ethanol in a nucleophilic substitution reaction with warm aqueous sodium hydroxide or potassium hydroxide. Here's the equation for this reaction:

$$CH_3CH_2Br + {}^{-}OH \xrightarrow{reflux} CH_3CH_2OH + Br^{-}$$

Here's how it happens:



1. The $C^{\delta+}$ from a polar C–Br bond attracts a lone pair of electrons from an OH^- ion.

3. The C–Br bond breaks heterolytically — both the electrons are taken by the Br.

4. A new bond forms between the C and the OH^- ion.

2. The OH^- ion acts as a nucleophile — it provides a pair of electrons for the $C^{\delta+}$.

5. The Br^- falls off as the OH^- bonds to the carbon.

2. Hydrolysis with water

The water molecule is a weak nucleophile, but it will eventually substitute for the halogen — it's just a much slower reaction than the one using a warm aqueous alkali. You get an alcohol produced again. The general equation is:

$$RX + H_2O \rightarrow ROH + H^{+} + X^{-}$$

Exam Tip
You must draw the curly arrows coming from the lone pair of electrons or from the bond.
If you don't, you won't get the marks for the mechanism in the exam.

Tip: This reaction is usually called hydrolysis, even though it's ${}^{-}OH$ ions from the alkali that are reacting, not water molecules.
That's because the product is the same as when you use water as a nucleophile (see below).

Tip: The C–F bond in fluoroalkanes is very strong (see page 256), so they can't be hydrolysed.

Tip: Refluxing is a method for heating a reaction to boiling point without losing volatile solvents, reactants or products (see page 279).

Tip: When you're drawing mechanisms make sure the charges balance. That way you'll know if you've lost track of any electrons along the way. In this example, the left-hand side has one negative charge on the hydroxide ion and the right-hand side has one negative charge from a bromide ion — so it's balanced.

Example

Bromoethane reacts slowly with water in a hydrolysis reaction to form ethanol. The equation for this reaction is:

$$CH_3CH_2Br + H_2O \rightarrow CH_3CH_2OH + H^+ + Br^-$$

Bond enthalpy and hydrolysis

How quickly different haloalkanes are hydrolysed depends on bond enthalpy — see page 168 for more on this. Weaker carbon-halogen bonds break more easily — so they react faster. Iodoalkanes have the weakest bonds, so they hydrolyse the fastest. Fluoroalkanes have the strongest bonds, so they're the slowest at hydrolysing (see Figure 2).

Tip: If you've got a molecule with more than one halogen in it, the halogen with the lowest bond enthalpy will get replaced first.

Bond	Bond Enthalpy (kJ mol⁻¹)
C–F	467
C–Cl	346
C–Br	290
C–I	228

Faster hydrolysis as bond enthalpy decreases (the bonds are getting weaker).

Figure 2: *Carbon-halogen bond enthalpies.*

Tip: To hydrolyse haloalkanes with high bond enthalpies you need to use harsher reaction conditions — for example, a higher temperature.

Comparing hydrolysis rates of haloalkanes

PRACTICAL ACTIVITY GROUP 7

You saw on the last page that when haloalkanes are mixed with water they will be slowly hydrolysed to form alcohols. This is the overall reaction:

$$RX + H_2O \rightarrow ROH + H^+ + X^-$$

If you put silver nitrate solution in the mixture too, the silver ions will react with the halide ions as soon as they form, giving a silver halide precipitate (see pages 153-154). This is the equation for that reaction:

$$Ag^+_{(aq)} + X^-_{(aq)} \rightarrow AgX_{(s)}$$

Tip: You use water as the nucleophile in this reaction — if you used an alkali the hydroxide ions would react with the silver nitrate to form a precipitate and mess up your results.

You can use this reaction to compare the reactivities of different haloalkanes. To do this, set up four flasks each containing the same amount of a different haloalkane, ethanol (as a solvent) and dilute silver nitrate solution.
You can 'measure' the rates of the reactions by timing how quickly each silver halide is precipitated, using the good old 'timing how long it takes the cross to disappear' method (not its official name...). Just stick a piece of paper with a cross on it under each flask and measure how long it takes until you can't see the cross any more (see Figure 3).

Tip: Remember to always do a risk assessment before you carry out any experiments in class.

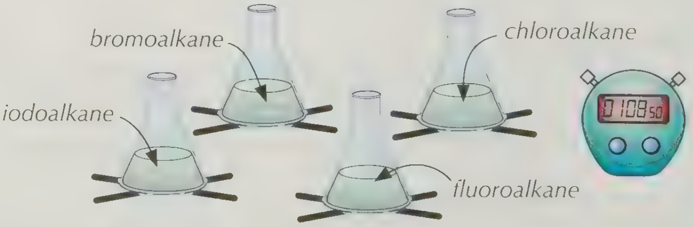


Figure 3: *Experimental set-up for measuring the rate of reaction of hydrolysis.*

Tip: The hydrolysis of haloalkanes by water can be very slow. So, you can warm all the reaction flasks to the same temperature to make the reactions in this experiment occur more quickly.

If all the conditions are the same (e.g. temperature, concentration of reactants, the carbon skeleton of the haloalkane, etc.), then you'll find that iodoalkanes react the fastest to form a precipitate, bromoalkanes are a bit slower to react, and chloroalkanes take ages to form a precipitate. Fluoroalkanes aren't hydrolysed at all. These observations match what you know about the bond enthalpies of the different carbon-halogen bonds (see last page).

Identifying unknown haloalkanes

PRACTICAL ACTIVITY GROUP 7

Sometimes, you can't use the relative reaction rates to identify the halogen present in a haloalkane. This may be the case if you only have one sample, or if you have samples where the carbon chains are different. Instead, you react a sample of the haloalkane in a test tube with water in the presence of silver nitrate solution and ethanol. The colour of the precipitate that forms will tell you what halogen is present in the haloalkane — yellow means it's an iodoalkane, cream means it's a bromoalkane and white means it's a chloroalkane (see Figures 4 and 6). The method for the experiment is similar to the one on the previous page.

Example

Three haloalkanes are labelled A, B and C. One is an iodoalkane, one is a bromoalkane and one is a chloroalkane. You can distinguish between them by comparing the colours of the precipitates formed when a sample of each haloalkane is warmed with water in the presence of silver nitrate and ethanol. The set-up for the reaction is shown in Figure 5.

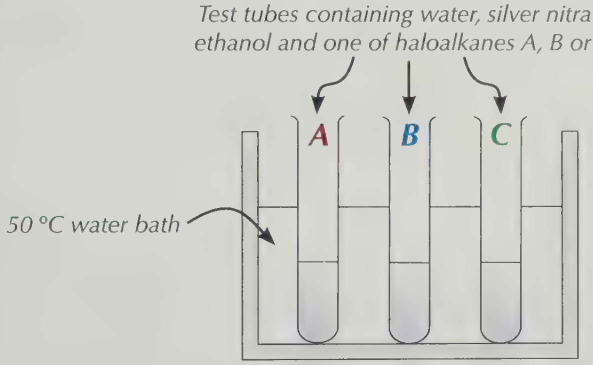

Test tubes containing water, silver nitrate, ethanol and one of haloalkanes A, B or C.
A
B
C
50 °C water bath

Figure 5: *The set-up of an experiment to determine the identity of the halogen in three unknown haloalkanes.*

The identity of each haloalkane can be determined once a precipitate has formed in each of the test tubes.

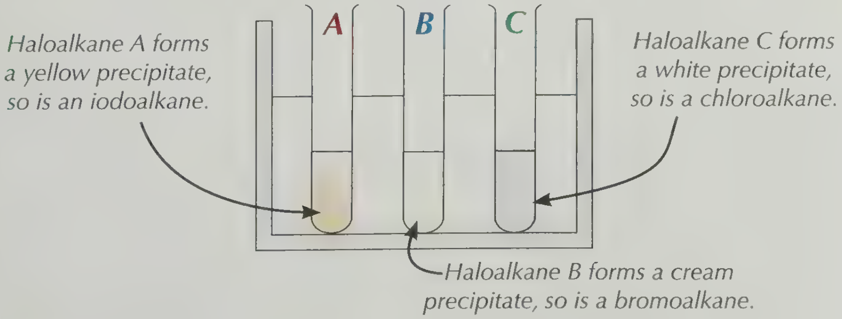

A
B
C
Haloalkane A forms a yellow precipitate, so is an iodoalkane.
Haloalkane C forms a white precipitate, so is a chloroalkane.
Haloalkane B forms a cream precipitate, so is a bromoalkane.

Figure 6: *The colours of the precipitates formed when different haloalkanes are reacted with water in the presence of silver nitrate and ethanol.*

Tip: You can only be sure that the identity of the halogen is what influences the relative rate of reaction between each sample if you keep everything else the same.

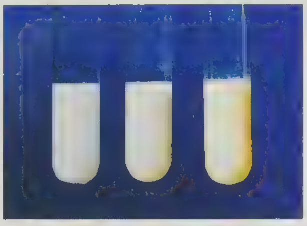


Figure 4: *The result of adding silver nitrate solution to a chloroalkane (left), a bromoalkane (middle) and an iodoalkane (right).*

Tip: You can't just use the difference in reaction rates to identify the haloalkanes. If their carbon skeletons are different, or each molecule contains different numbers of halogen atoms, then this will affect the reaction rate as well.

Tip: You may need to look at the rates as well as the colours of the precipitates to successfully identify an unknown haloalkane.

Tip: Always do a risk assessment before you do any experiments in the lab to make sure you're working safely. For example, silver nitrate solution can irritate your skin and eyes, so you should wear a lab coat, gloves and goggles if you do an experiment like this in class.

Tip: Remember that skeletal formulas only show the bonds of the carbon skeleton and any functional groups on the molecule. The hydrogen atoms aren't shown at all.

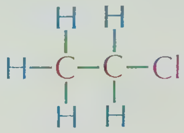
Practice Questions — Application

Q1 Draw skeletal formulas for the following haloalkanes:

a) 1-bromobutane b) 2,3-difluoropentane

c) 1-bromo-2-chloropropane d) 1-iodohexane

Q2 Draw the mechanism for the hydrolysis of chloroethane by warm aqueous sodium hydroxide. The structure of chloroethane is shown below.



$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & - & C & - & C & - & Cl \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

Exam Tip
When drawing any mechanism, double-check that you've drawn all the necessary curly arrows, lone pairs and partial charges. You'll lose marks in the exam if you've missed one out.

Q3 Which of the following reactions, **A**, **B** or **C**, would be quickest? Explain your answer.

A $CH_3CH_2Cl + H_2O \rightarrow CH_3CH_2OH + HCl$

B $CH_3CH_2Br + H_2O \rightarrow CH_3CH_2OH + HBr$

C $CH_3CH_2I + H_2O \rightarrow CH_3CH_2OH + HI$

Q4 Three unknown haloalkanes, A, B and C, are reacted separately with water in the presence of silver nitrate solution and ethanol. The time taken for an 'X' on a piece of card behind each test tube to disappear is recorded. The haloalkanes all have the same carbon skeleton, but one is a chloroalkane, one is a bromoalkane and one is an iodoalkane. Apart from the identity of the haloalkane, all the other variables in each reaction are kept the same. The results of each reaction are shown in the table below.

Haloalkane	Time for X to disappear (s)
A	240
B	7
C	567

a) Use the table to identify the halogen present in each of the haloalkanes, A, B and C.

b) Explain why variables such as the concentration of reactants need to be kept the same between the different samples.

Practice Questions — Fact Recall

Q1 What property of haloalkanes causes them to be attacked by nucleophiles?

Q2 Briefly describe what a nucleophilic substitution reaction is.

Q3 Name a substance that you could react with bromoethane to produce ethanol.

Q4 Explain why fluoroalkanes are hydrolysed more slowly than other haloalkanes.

Q5 Write an equation for the reaction of bromoethane with hydroxide ions.

Q6 Describe a test you could carry out to identify whether a haloalkane is a chloroalkane, a bromoalkane or an iodoalkane.

Tip: There's loads of stuff about how to plan experiments and analyse data in the Practical Skills section on pages 5-23.

5. Chlorofluorocarbons

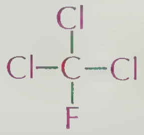
Chlorofluorocarbons are a family of haloalkanes. They were once used for loads of things, before it was discovered that they were destroying the ozone layer...

Chlorofluorocarbons

Chlorofluorocarbons (CFCs) are well-known haloalkanes. They contain only chlorine, fluorine and carbon — all the hydrogens have been replaced. They're very stable, volatile, non-flammable and non-toxic. They were used a lot — e.g. in fridges, aerosol cans, dry cleaning and air-conditioning — until scientists realised they were destroying the ozone layer.

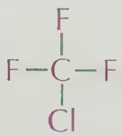
Examples

Trichlorofluoromethane and chlorotrifluoromethane are both CFCs.



$Cl-\underset{F}{\overset{Cl}{C}}-Cl$

trichlorofluoromethane



$F-\underset{Cl}{\overset{F}{C}}-F$

chlorotrifluoromethane

Chlorofluorocarbons and the ozone layer

The **ozone layer** is in a layer of the atmosphere called the stratosphere. It contains most of the atmosphere's ozone molecules, O_3, and acts as a chemical sunscreen. It absorbs a lot of the ultraviolet radiation which can cause sunburn or even skin cancer. Ozone's formed naturally when an oxygen molecule is broken down into two free radicals by ultraviolet radiation:

$$O_2 + h\nu \rightarrow O + O$$

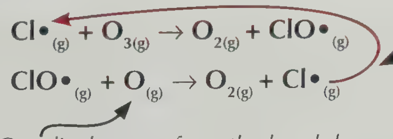
The free radicals attack other oxygen molecules, forming ozone:

$$O_2 + O \rightarrow O_3$$

In the 1970s and 1980s, scientists discovered that the ozone layer above Antarctica was getting thinner — in fact, it was thinning very rapidly. The ozone layer over the Arctic has been found to be thinning too. These 'holes' in the ozone layer are bad because they allow more harmful UV radiation to reach the Earth. The 'holes' are formed because when CFCs travel up into the upper atmosphere they absorb high-energy UV radiation and split to form chlorine free radicals. For example:

$$CF_2Cl_{2(g)} + h\nu \rightarrow CF_2Cl\bullet_{(g)} + Cl\bullet_{(g)}$$

These free radicals catalyse the destruction of ozone — they destroy ozone molecules and are then regenerated to destroy more ozone. One chlorine atom can destroy 10 000 ozone molecules before it forms a stable compound. Here's what happens:



$$Cl\bullet_{(g)} + O_{3(g)} \rightarrow O_{2(g)} + ClO\bullet_{(g)}$$

$$ClO\bullet_{(g)} + O_{(g)} \rightarrow O_{2(g)} + Cl\bullet_{(g)}$$

The chlorine free radical is regenerated. It goes straight on to attack another ozone molecule.

The O radical comes from the breakdown of oxygen by ultraviolet radiation.

Because the Cl• free radical is regenerated, it only takes one little chlorine free radical to destroy loads of ozone molecules. So, the overall reaction is...

$$O_{3(g)} + O_{(g)} \rightarrow 2O_{2(g)}$$

... and Cl• is the catalyst.

Learning Objectives:

- Be able to explain how halogen radicals are produced by the action of ultraviolet (UV) radiation on CFCs in the upper atmosphere.
- Understand how halogen radicals can catalyse the breakdown of the Earth's protective ozone layer.
- Be able to write equations to represent the production of halogen radicals and the catalysed breakdown of ozone by Cl• and other radicals, e.g. •NO.

Specification Reference 4.2.2

Tip: The hν in the first equation is the notation for a quantum of UV radiation — a photon. It just means that the reaction needs to be initiated by electromagnetic radiation.

Tip: CFCs are really stable, so they don't get broken down in the lower atmosphere. Instead they can travel all the way up to the ozone layer, where they wreak havoc.

Tip: The chlorine radicals are homogeneous catalysts because they're in the same phase as the ozone molecules.

Nitrogen oxides and the ozone layer

Chlorine radicals often get blamed for destroying the ozone layer, but there are other radicals that are also catalysing the breakdown of ozone. For example, NO• free radicals from **nitrogen oxides** destroy ozone too. Nitrogen oxides are produced by car and aircraft engines, and thunderstorms. NO• free radicals affect ozone in the same way as chlorine radicals.

The reactions showing how ozone is broken down can be represented by equations where **R** represents any radical, for example Cl• or NO•.

$$\mathrm{R + O_3 \rightarrow RO + O_2}$$
$$\mathrm{RO + O \rightarrow R + O_2}$$

In both cases, the free radicals act as **catalysts** for the destruction of the ozone. The overall reaction is:

$$\mathrm{O_3 + O \rightarrow 2O_2}$$

Tip: NO• and Cl• aren't the only culprits — free radicals are produced from haloalkanes containing other halogens too.

Alternatives to CFCs

Scientific evidence showed that the advantages of CFCs couldn't outweigh the environmental problems they were causing, so they were banned. The Montreal Protocol of 1987 was an international treaty to phase out the use of CFCs and other ozone-destroying haloalkanes by the year 2000. There were a few permitted uses, such as in medical inhalers and in fire extinguishers used in submarines. Scientists supported the treaty, and worked on finding alternatives to CFCs.

Tip: Scientific evidence was used as a basis by governments to draw up an international agreement that banned the use of CFCs.

HOW SCIENCE WORKS

HCFCs and HFCs

HCFCs (hydrochlorofluorocarbons) and HFCs (hydrofluorocarbons) are being used as temporary alternatives to CFCs until safer products are developed. Hydrocarbons are also used.

The problem with CFCs is that they hang around in the atmosphere causing disruption for ages — it takes an average of 90 years for them to leave the atmosphere. HCFCs are broken down in the atmosphere in 10-20 years. They still damage the ozone layer, but their effect is much smaller than that of CFCs. HFCs are broken down in the atmosphere too and they don't contain chlorine, so they don't affect the ozone layer.

Unfortunately, HFCs and HCFCs are greenhouse gases (see page 261) — they contribute towards the warming of the Earth. Some hydrocarbons are being used in fridges, but these are greenhouse gases too. Nowadays, most aerosols have been replaced by pump spray systems or use nitrogen as the propellant. Many industrial fridges and freezers now use ammonia as the coolant gas, and carbon dioxide is used to make expanded polymers.

These substances do have drawbacks, but they're currently the least environmentally damaging of all the alternatives. The ozone holes still form in the spring but are slowly shrinking — so things are looking up.

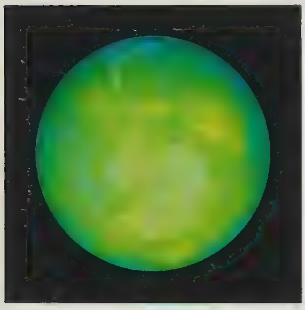


Figure 1: *Satellite image of the ozone layer over Antarctica in 1979.*

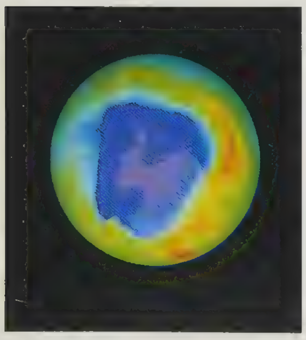


Figure 2: *Satellite image of the ozone layer over Antarctica in 2013. The 'hole' is shown by the blue area.*

Practice Questions — Fact Recall

Q1 What is a chlorofluorocarbon (CFC)?

Q2 Write equations to show how chlorofluorocarbons can catalyse the breakdown of ozone in the stratosphere.

Q3 Name one type of chemical that is used as an alternative to CFCs.

6. Global Warming

Global warming, the greenhouse effect and climate change seem to crop up in every subject, at every level. Here's the chemistry spin on them, including how chemists are involved in measuring, monitoring and fighting back.

Learning Objectives:

- Know that atmospheric gases containing C=O, O–H and C–H bonds (e.g. H_2O, CO_2 and CH_4) are able to absorb infrared radiation.
- Understand why H_2O, CO_2 and CH_4 are suspected to be linked to global warming.
- Understand how energy usage has changed as a result of the suspected link between H_2O, CO_2 and methane with global warming.

Specification Reference 4.2.4

Greenhouse gases

Some of the electromagnetic radiation from the Sun reaches the Earth and is absorbed. The Earth then re-emits it as infrared radiation (heat). Various gases in the **troposphere** (the lowest layer of the atmosphere) absorb some of this infrared radiation... and re-emit it in all directions — including back towards Earth, keeping us warm (see Figure 1). This is called the '**greenhouse effect**' (even though a real greenhouse doesn't actually work like this, annoyingly).

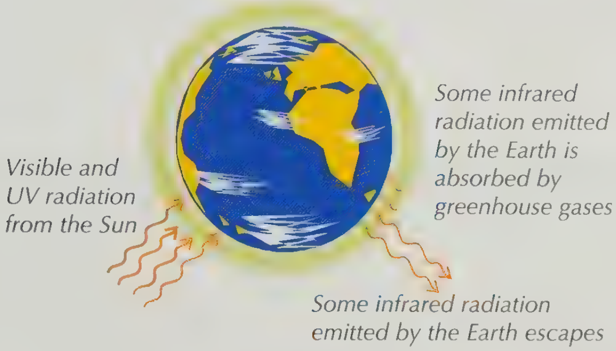

Visible and UV radiation from the Sun
Some infrared radiation emitted by the Earth is absorbed by greenhouse gases
Some infrared radiation emitted by the Earth escapes

Figure 1: *The greenhouse effect.*

The main **greenhouse gases** are water vapour, carbon dioxide and methane. The C=O, O–H and C–H bonds in these molecules absorb infrared (IR) radiation (see page 267) and this makes the bonds in the molecule vibrate more. This extra energy is passed on to other molecules in the air by collisions, giving the other molecules more kinetic energy and raising the overall temperature.

Not all greenhouse gases contribute the same amount to the greenhouse effect. The contribution of any particular gas depends on a number of factors, including:

- How much IR radiation one molecule of the gas absorbs.
- How much of that gas there is in the atmosphere.
- How long the gas stays in the atmosphere for.

Example

One methane molecule traps far more heat than one carbon dioxide molecule, but there's much less methane in the atmosphere, so its overall contribution to the greenhouse effect is smaller. A molecule of methane also spends much less time in the atmosphere, before it's broken down, than a molecule of carbon dioxide.

Figure 2: *Methane is released from cows...*

What is global warming?

Over the last 150 years or so, the world's human population has shot up and we've become more industrialised. We've been burning fossil fuels, releasing tonnes of CO_2, and we've been chopping down forests which used to absorb CO_2 by photosynthesis.

Methane levels have also risen as we've grown more food. Cows produce large amounts of methane (from both ends). Paddy fields, in which rice is grown, kick out a fair bit of it too.

Figure 3: *...and from paddy fields (fields where rice is grown).*

Tip: The concentration of water vapour in the atmosphere stays roughly constant because when there's too much, it falls as rain.

These human activities have caused a rise in greenhouse gas concentrations, which enhances the greenhouse effect. More heat is being trapped and the Earth is getting warmer — this is **global warming**.

Evidence for global warming

HOW SCIENCE WORKS

Scientists have collected data to provide evidence for if and why global warming and climate change are happening, e.g. from analysing air samples and seawater samples.
The evidence shows that the Earth's average temperature has increased dramatically in the last 50 years, and that CO_2 levels have increased at the same time — see Figure 4.

Tip: You don't need to memorise this graph — just notice that whenever atmospheric CO_2 increases, the temperature difference also increases. This is a correlation. See pages 17-18 for more on correlation.

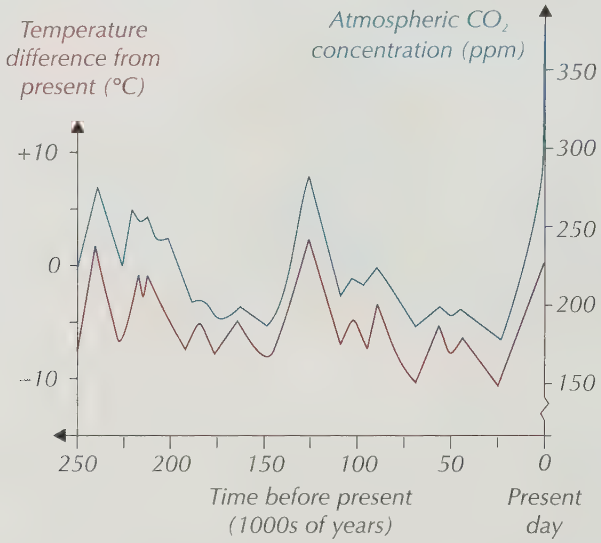


Figure 4: *Graph showing the correlation between atmospheric CO_2 concentration and temperature.*

The correlation between CO_2 and temperature is pretty clear, but there's been debate about whether rising carbon dioxide levels have caused the recent temperature rise. Just showing a correlation doesn't prove that one thing causes another — there has to be a plausible mechanism for how one change causes the other (in this case, the explanation is the enhanced greenhouse effect). There's now a consensus among climate scientists that the link is causal, and that recent warming is largely anthropogenic — this means that human activities are to blame.

Tip: Don't get confused — the greenhouse effect isn't a bad thing. In fact, without it the Earth would be too cold for us to live on. The problem comes when the greenhouse effect is enhanced by adding more greenhouse gases to the atmosphere. This causes global warming, which is where all the problems come in.

Consequences of global warming

Global warming won't just make everywhere a bit warmer and affect the skiing — warmer oceans will expand and massive ice sheets in the polar regions could melt, causing sea levels to rise and leading to more flooding. The climate in any region of the world depends on a really complicated system of ocean currents, winds, etc. Global warming means there's more heat energy in the system. This could lead to stormier, less predictable weather. In some places there could be much less rainfall, with droughts and crop failures causing famines and forcing entire populations to become refugees. In other regions, increased rainfall and flooding could bring diseases like cholera.

Efforts to prevent global warming

HOW SCIENCE WORKS

Scientific evidence has persuaded governments to form a global agreement that climate change could be damaging for people, the environment and economies, and that we should try to **limit** it.

In 1997 the **Kyoto protocol** was signed — industrialised countries (including the UK) promised to reduce their greenhouse gas emissions to agreed levels. This agreement came to an end in 2012, and currently has no replacement, though many governments agree that they need to reduce CO_2 emissions by around 50% by 2050.

In the UK, the government has created policies to use more **renewable energy resources**, such as through wind and solar farms, in order to reduce the country's emissions. This has reduced the need for coal-burning power stations, which are a major source of carbon dioxide pollution and used to be one of the main sources of electricity in the UK. The government have also encouraged the use of more energy-efficient alternatives to everyday objects, such as energy-saving light bulbs and electric cars.

Tip: See pages 1-4 for more on how scientists collect evidence and use it to support their claims.

Figure 5: *Wind turbines use wind energy, a renewable energy resource, to generate electricity.*

Practice Questions — Fact Recall

Q1 What type of radiation do greenhouse gases absorb?

Q2 Name three greenhouse gases.

Q3 How is the greenhouse effect linked to global warming?

Q4 Explain why global warming is a problem.

Q5 How are governments working to limit global warming?

Section Summary

Make sure you know...

- How to use the IUPAC rules of nomenclature to name alcohols.
- What primary, secondary and tertiary alcohols are and how to spot them.
- That alcohols are polar molecules and are able to form hydrogen bonds.
- How hydrogen bonding affects the water solubility, volatility and boiling points of alcohols.
- That alcohols can undergo nucleophilic substitution reactions with halide ions to form haloalkanes.
- That water can be eliminated from alcohols to form a mixture of alkene products, and if these alkenes have *E*/*Z* isomers then both isomers will form.
- How to describe the combustion of alcohols.
- What aldehydes, ketones and carboxylic acids are.
- How to use the IUPAC rules of nomenclature to name aldehydes, ketones and carboxylic acids.
- That you can oxidise primary and secondary alcohols using acidified potassium dichromate(VI).
- How to oxidise primary alcohols to form aldehydes and carboxylic acids.
- How to oxidise secondary alcohols to form ketones.
- That tertiary alcohols can only be oxidised by burning.
- That you can use acidified potassium dichromate(VI) as a test to distinguish tertiary alcohols from primary and secondary alcohols.
- How to use the IUPAC rules of nomenclature to name haloalkanes.
- That carbon-halogen bonds are polar so they can be attacked by nucleophiles.
- That a nucleophile is an electron-pair donor.
- The basic mechanism for a nucleophilic substitution reaction.
- That haloalkanes can be hydrolysed by warm aqueous alkali or, much more slowly, by water.
- That hydrolysis of a haloalkane is a nucleophilic substitution reaction.
- The mechanism for the reaction of a haloalkane with a warm aqueous alkali.
- That the hydrolysis rate of haloalkanes depends on the bond enthalpy of the carbon-halogen bond.
- How you can compare the rate of hydrolysis of haloalkanes experimentally using water in the presence of silver nitrate and ethanol.
- How to identify different haloalkanes by observing the colour of the precipitate formed when the haloalkane is warmed with silver nitrate and ethanol.
- That CFCs are volatile, non-toxic, non-flammable and not very reactive.
- That CFCs produce halogen radicals in the upper atmosphere which catalyse the breakdown of the ozone layer.
- That other radicals, such as NO•, also catalyse the breakdown of ozone.
- How to write equations to show how radicals can catalyse the breakdown of ozone.
- That scientists are working to find less harmful alternatives to CFCs (e.g. hydrocarbons, HFCs and HCFCs).
- The mechanism behind the greenhouse effect.
- That atmospheric gases containing C=O, C–H and O–H bonds (such as CO_2, CH_4 and H_2O) can all absorb infrared (IR) radiation.
- That the rise in atmospheric levels of CO_2, CH_4 and H_2O is suspected to be linked to global warming, and energy use has changed as a result.

Exam-style Questions

1 When 2,2,4-trimethylpentan-3-ol is reacted with hot, concentrated phosphoric acid, how many different alkene products are formed?

A 1

B 2

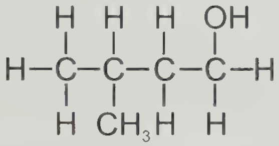
C 3

D 4

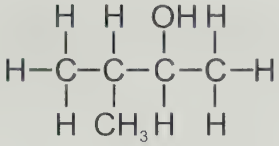
(1 mark)

2 Which of the following organic compounds can be refluxed with acidified potassium dichromate(VI) to form 3-methylbutanone?

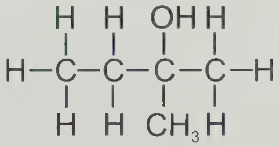
A



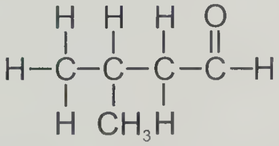
B



C



D



(1 mark)

3 Which of the following statements about global warming is correct?

A The correlation between rising carbon dioxide levels and rising global temperatures proves that carbon dioxide is causing global warming.

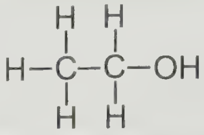
B The greenhouse effect is caused by increased levels of gases that absorb infrared radiation in the atmosphere.

C Global warming is largely man-made.

D The amount a greenhouse gas contributes to the greenhouse effect only depends on its concentration in the atmosphere.

(1 mark)

4 Ethanol is a simple alcohol that can be used as a solvent and as a starting point for many organic synthesis reactions. Its structure is shown below.



$$\mathrm{H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-OH}$$

(a) Ethanol can be made by reacting bromoethane with warm aqueous sodium hydroxide.

(i) Write the equation for this reaction.

(1 mark)

(ii) Draw the mechanism for the reaction between bromoethane and hydroxide ions.

(3 marks)

(iii) Ethanol can also be made by reacting iodoethane with warm aqueous sodium hydroxide. Which of the reactions would proceed more quickly? Explain your answer.

(2 marks)

(b) Ethanol is soluble in water.

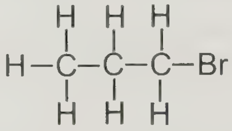
(i) Explain why ethanol is soluble in water.

(1 mark)

(ii) Explain why butan-1-ol is less soluble in water than ethanol.

(1 mark)

5 A scientist has synthesised a molecule — molecule **A**.
The molecule was synthesised by reacting ^{-}OH ions with 1-bromopropane.
The structure of 1-bromopropane is shown below.



$$\mathrm{H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-Br}$$

(a) Draw the displayed structure of molecule **A** and give its systematic name.

(2 marks)

(b) Suggest what reagents and conditions would be needed to produce a carboxylic acid from molecule **A**.

(2 marks)

6 CFCs are molecules that have been linked to the destruction of ozone in the upper atmosphere.

(a) Explain why the ozone layer is an important part of the atmosphere.

(1 mark)

(b) What role do CFCs play in the destruction of ozone?

(2 marks)

(c) NO• is another species that has been linked to the breakdown of ozone molecules. Write equations to show how ozone can be broken down in the presence of NO•. You don't need to show how NO• is formed, but you should include an overall equation for the reaction.

(3 marks)

1. Infrared Spectroscopy

Infrared spectroscopy is an analytical technique which can help you to identify a compound. The bonds of different functional groups absorb different frequencies of infrared light. This means we can use an infrared spectrum of a molecule to identify its functional groups.

The basics

In **infrared (IR) spectroscopy**, a beam of IR radiation is passed through a sample of a chemical. The IR radiation is absorbed by the covalent bonds in the molecules, increasing their vibrational energy (they vibrate more). Bonds between different atoms absorb different frequencies of IR radiation. Bonds in different places in a molecule absorb different frequencies too — so the O–H bond in an alcohol and the O–H in a carboxylic acid absorb different frequencies. Figure 1 shows what frequencies different bonds absorb — you don't need to learn this data, but you do need to understand how to use it. Wavenumber is the measure used for the frequency (it's just 1/wavelength).

Bond	Where it's found	Frequency / Wavenumber (cm^{-1})
C–C	alkanes, alkyl chains	750 – 1100
C–X	haloalkanes	500 – 800
C–F	fluoroalkanes	1000 – 1350
C–O	alcohols, carboxylic acids	1000 – 1300
C=C	alkenes	1620 – 1680
C=O	aldehydes, ketones, carboxylic acids	1630 – 1820
C–H	most organic molecules	2850 – 3100
O–H	carboxylic acids	2500 – 3300 (broad)
O–H	alcohols	3200 – 3600

Figure 1: *Infrared absorption for different bonds in organic molecules.*

An infrared spectrometer produces a graph, known as a spectrum, that shows you what frequencies of radiation the bonds in a molecule are absorbing. So you can use it to identify the functional groups in the molecule. The peaks show you where radiation is being absorbed — the 'peaks' on IR spectra are upside down.

Learning Objectives:

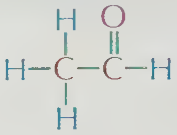
- Know that infrared (IR) radiation causes covalent bonds to vibrate more and absorb energy.
- Be able to use the infrared spectrum of an organic compound to identify an alcohol from an absorption peak of the O–H bond, an aldehyde or ketone from an absorption peak of the C=O bond, and a carboxylic acid from an absorption peak of the C=O bond and a broad absorption peak of the O–H bond.
- Be able to interpret and predict the infrared spectrum of a familiar or unfamiliar substance using supplied data.
- Know how infrared spectroscopy is used to monitor gases causing air pollution (e.g. CO and NO from car emissions) and in modern breathalysers.

Specification Reference 4.2.4

Exam Tip
You'll get a table like the one in Figure 1 on the data sheet in your exam. So there's no need to memorise all those numbers — yay.

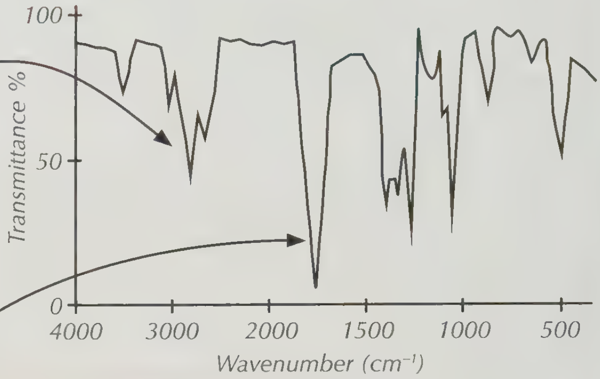
Example — **Maths Skills**

Here is the structure and the infrared spectrum of ethanal:



$$H-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle O}{\|}}{C}-H$$

ethanal



The absorption at about 3000 cm^{-1} is caused by the C–H bonds.

This strong, sharp absorption at about 1700 cm^{-1} shows you there's a C=O bond.

Tip: Most organic molecules will have loads of C–H bonds in them. This means the region at ~3000 cm^{-1} on an IR spectrum isn't always very useful when it comes to identifying what an organic molecule could be.

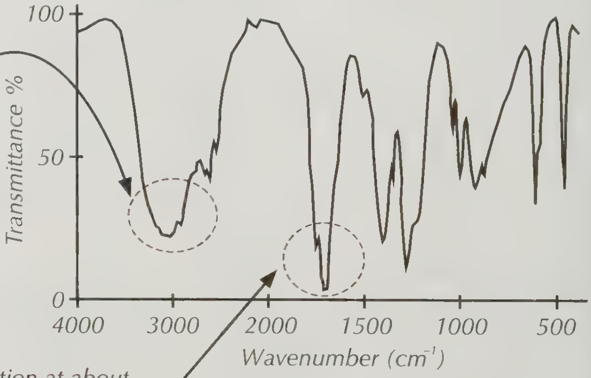
Interpreting IR spectra

Infrared spectroscopy is a powerful tool for identifying molecules. By looking at the peaks in the IR spectrum of an unknown molecule, you can identify what functional groups it's likely to contain.

Example — **Maths Skills**

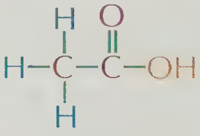
An unknown compound has $M_r = 60$. Its infrared spectrum is shown below:

This medium intensity, broad absorption at about 3000 cm^{-1} shows you there's an O–H bond in a carboxylic acid group.



This strong, sharp absorption at about 1720 cm^{-1} shows you there's a C=O bond.

The peaks on the IR spectrum tell you that the molecule must contain a carboxylic acid group (this accounts for the C=O group and the carboxylic acid O–H group). There's only one carboxylic acid with $M_r = 60$ — ethanoic acid.



$$H-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle O}{\|}}{C}-OH$$

ethanoic acid

Tip: When you're reading an infrared spectrum, always double-check the scale. The wavenumbers increase from right to left — don't get caught out.

Tip: You can use infrared spectroscopy to tell if a functional group has changed during a reaction. For example, if you oxidise an alcohol to an aldehyde you'll see the O–H absorption disappear from the spectrum, and a C=O absorption appear.

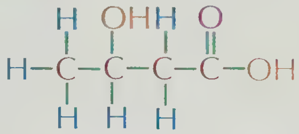
Predicting infrared spectra

As well as using an infrared spectrum to identify an unknown molecule, you can use the structure of a molecule to predict what peaks will be present in its infrared spectrum. All you have to do is work out what functional groups are in the molecule, and then use the values on the data sheet to predict roughly where the absorption peaks will be.

Tip: You won't be able to predict exactly where each peak will be, but a rough range is fine.

Example **Maths Skills**

Here is the structure of 3-hydroxybutanoic acid:



The molecule contains C–C, C–H, C–O, O–H (alcohol), C=O and O–H (carboxylic acid) bonds that are all able to absorb infrared radiation.

Once you've identified all the different bonds in the molecule, all that's left to do is use your data sheet to look up where the peaks for each of these bonds appear on an infrared spectrum.

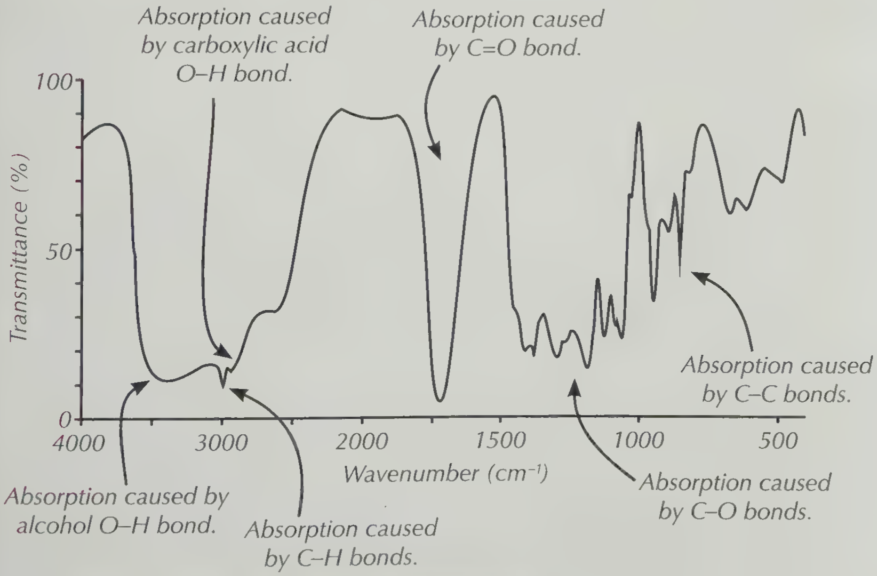
So, the infrared spectrum of 3-hydroxybutanoic acid is likely to have peaks at the following wavenumbers:

Exam Tip
If you're asked to predict what the infrared spectrum for a molecule will look like, it helps to draw out the displayed structure of the molecule. This will help to make sure you don't miss out any bonds when working out what peaks will be in the spectrum.

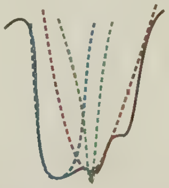
Bond	Frequency / Wavenumber (cm^{-1})
C–C	750 – 1100
C–O	1000 – 1300
C=O	1630 – 1820
C–H	2850 – 3100
O–H (carboxylic acid)	2500 – 3300 (broad)
O–H (alcohol)	3200 – 3600

Tip: Again, you don't have to remember all these numbers. The data sheet, which you'll be given in your exam, will tell you the wavenumbers of all the peaks you need to know.

In fact, the infrared spectrum of 3-hydroxybutanoic acid looks like this:



Tip: It's hard to identify each of the peaks on this spectrum, as some of them appear at very similar wavenumbers. The alcohol O–H peak, the C–H peak and the carboxylic acid O–H peak all overlap and so are merged together in the spectrum:



Applications of IR spectroscopy

As well as being used by scientists to identify unknown compounds, IR spectroscopy also has uses outside the lab.

HOW SCIENCE WORKS

Breathalysers

If a person's suspected of drink-driving, they're breathalysed. First, a very quick test is done by the roadside — if it says that the driver's over the limit, they're taken into a police station for a more accurate test using infrared spectroscopy. The amount of ethanol vapour in the driver's breath is found by measuring the intensity of the peak corresponding to the C–H bond in the IR spectrum. It's chosen because it's not affected by any water vapour in the breath. The IR spectrum from the breathalyser test is kept and can be used as evidence in court during the offender's trial.

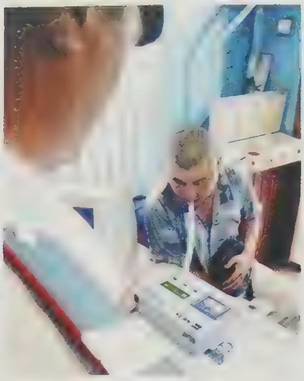


Figure 2: *A man undergoing a drink-driving breath test at a police station.*

Tip: You can't use the intensity of the O–H bond peak to measure the amount of alcohol in a breath sample. This is because water also contains O–H bonds, so the size of this peak will be affected by how much water is in the breath sample as well as how much alcohol there is.

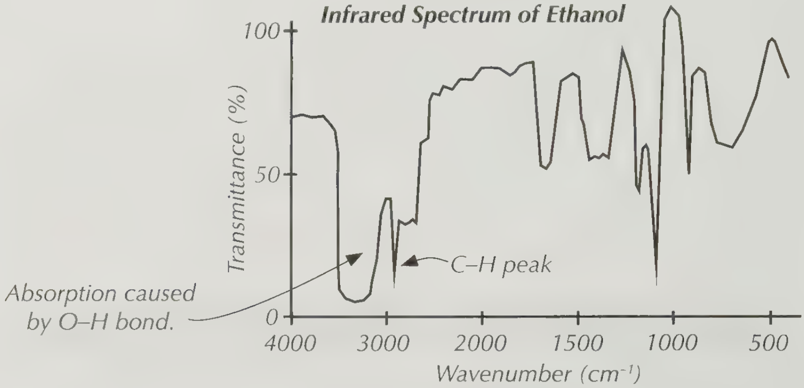


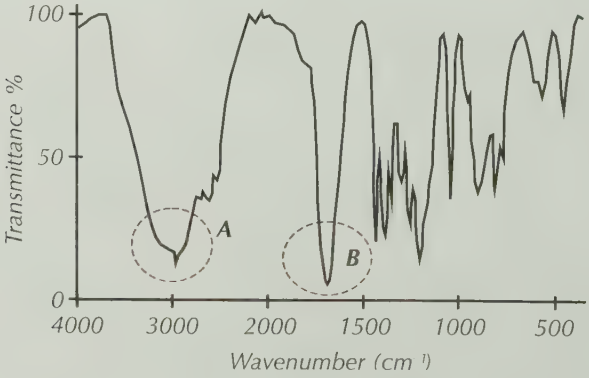
Figure 3: *The infrared absorption spectrum of ethanol.*

Monitoring pollutants

Infrared spectroscopy is used to monitor the concentrations of **polluting gases** in the atmosphere. These include carbon monoxide (CO) and nitrogen monoxide (NO), which are both present in car emissions. The intensity of the peaks corresponding to the C≡O or N=O bonds can be studied to monitor their levels.

Practice Questions — Application

Q1 The spectrum below is the infrared spectrum of a carboxylic acid with $M_r = 74$.



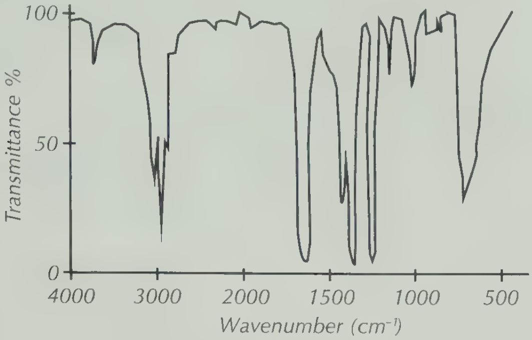
a) Identify the bonds that create the peaks marked **A** and **B** in the diagram.

b) Draw the displayed formula of the molecule.

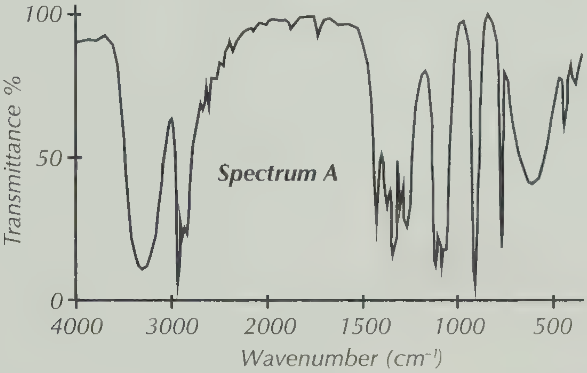
Tip: You can use the data table on page 267 to help you with all of these questions.

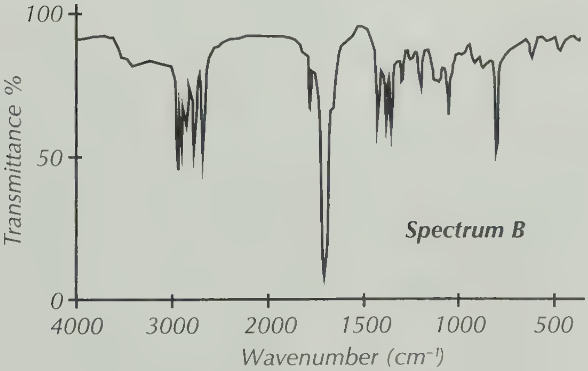
Tip: Remember that displayed formulas have to show all of the bonds present in a molecule.

Q2 The infrared spectrum of an unknown molecule is shown below. Use the spectrum to identify one important bond that can be found in the molecule.

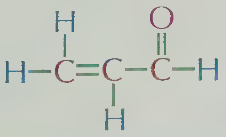


Q3 One of the infrared spectra below is the infrared spectrum of propan-2-ol. Identify which spectrum (**A** or **B**) it is.





Q4 Predict the wavenumbers of the peaks you would expect to see in the infrared spectrum of the molecule prop-2-enal:



$$\mathrm{H{-}\overset{H}{C}{=}\underset{H}{C}{-}\overset{O}{\overset{\|}{C}}{-}H}$$

Exam Tip

Remember — if you're asked to predict the spectrum of a molecule in the exam, it may help to draw the molecule out so it's easy to spot the functional groups and other bonds.

Practice Questions — Fact Recall

Q1 Give a brief explanation of how an infrared spectrum is created.

Q2 Describe one application of infrared spectroscopy.

2. Mass Spectrometry

Learning Objectives:

- Be able to use a mass spectrum of an organic compound to identify the molecular ion peak and hence to determine molecular mass.
- Be able to analyse fragmentation peaks in a mass spectrum to identify parts of structures.

Specification Reference 4.2.4

This topic deals with another analytical technique — mass spectrometry. Mass spectrometry uses the mass of a compound to identify it. It's not quite as simple as it sounds though... you'll have to learn about something called 'fragmentation'. Read on to find out more...

Finding relative molecular mass

You saw on page 46 how you can use a **mass spectrum** showing the relative isotopic abundances of an element to work out its relative atomic mass. You need to make sure you can remember how to do this. You can also get mass spectra for molecular samples.

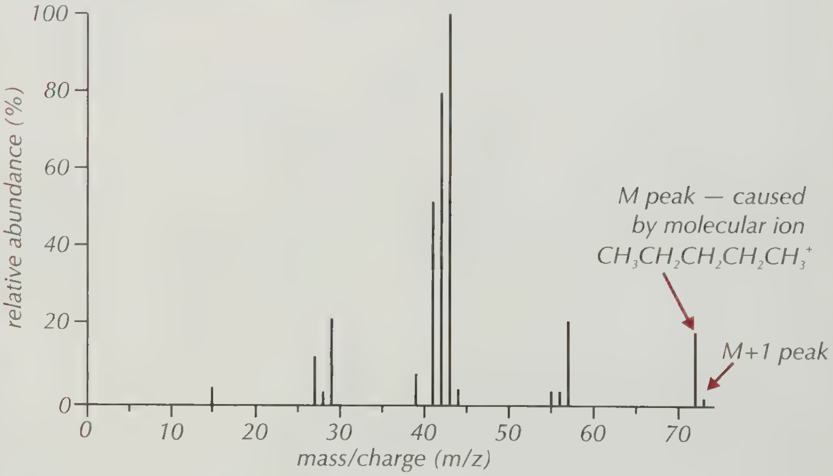
A mass spectrum is produced by a mass spectrometer. The molecules in the sample are bombarded with electrons and a molecular ion, $M^+_{(g)}$, is formed when the bombarding electrons remove an electron from the molecule. On a mass spectrum the *y*-axis gives the abundance of the ions, often as a percentage. The *x*-axis is the mass/charge ratio. This is just the molecular mass of the ion divided by its charge.

Figure 1: Mass spectrometer.

To find the relative molecular mass of a compound you look at the molecular ion peak (the M peak). For the spectra that you'll see, the M peak is the one with the highest mass/charge ratio, ignoring any M+1 peak (see below). The mass/charge value of the molecular ion peak is the molecular mass of the compound (assuming the ion has +1 charge, which it normally will have).

Example — Maths Skills

Here's the mass spectrum of pentane ($CH_3CH_2CH_2CH_2CH_3$).



Its M peak is at 72 — so the compound's M_r is 72.

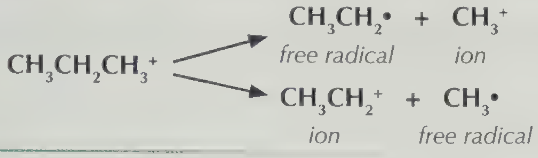
Tip: The M+1 peak arises mainly because, in a given sample, a small percentage of the organic molecules will contain atoms of the carbon isotope carbon-13. If you're given a question containing a spectrum with an M+1 peak, you can just ignore it when working out the M_r of the molecule from its mass spectrum.

Fragmentation

The bombarding electrons make some of the molecular ions break up into fragments. The fragments that are ions show up on the mass spectrum, making a fragmentation pattern. **Fragmentation patterns** are actually pretty cool because you can use them to identify molecules and even their structure.

Example

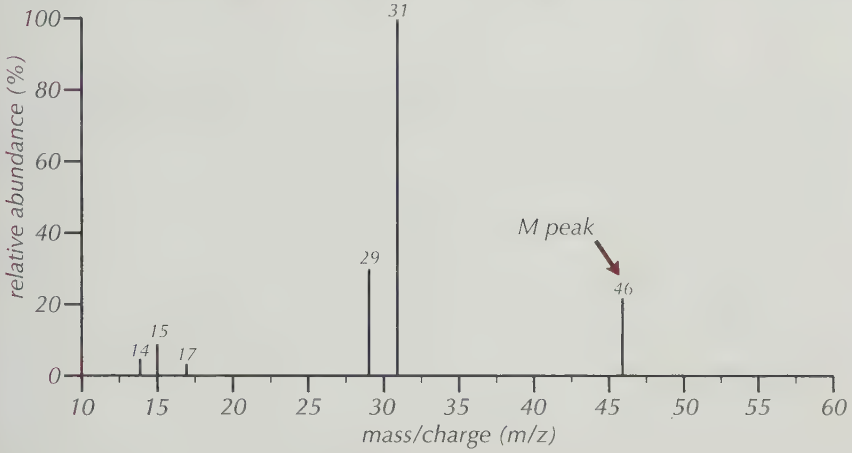
For propane ($CH_3CH_2CH_3$), the molecular ion is $CH_3CH_2CH_3^+$, and the fragments it breaks into include CH_3^+ (M_r = 15) and $CH_3CH_2^+$ (M_r = 29).



To work out the structural formula, you've got to work out what ion could have made each peak from its *m/z* value. (You can assume that the *m/z* value of a peak matches the mass of the ion that made it.)

Example — **Maths Skills**

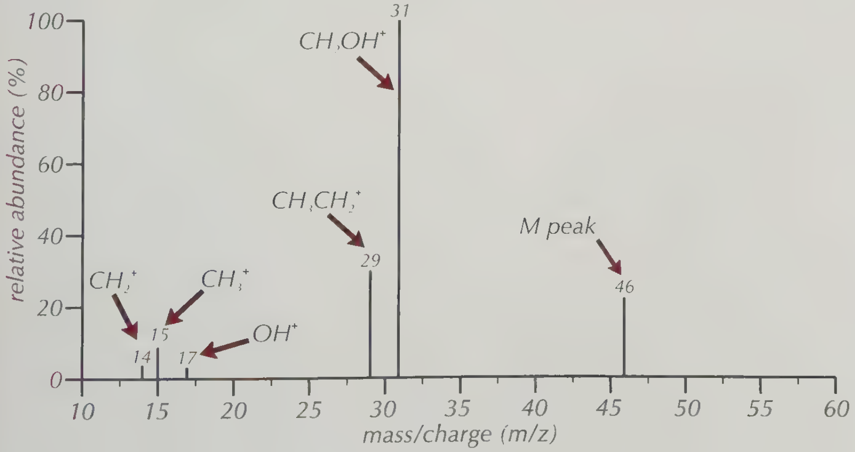
The mass spectrum below is for a molecule with the molecular formula C_2H_6O. Use the mass spectrum to work out the structure of the molecule.



First you need to identify the fragments — you can use Figure 2 to help you identify some common ions.

- This molecule's got a peak at *m/z* = 15, so it's likely to have a CH_3 group. It has a peak at *m/z* = 29, so it's likely to have a CH_3CH_2 group. It's also got a peak at *m/z* = 17, so it's likely to have an OH group.
- To find the other fragments you just have to add combinations of 12 (the mass of carbon), 1 (the mass of hydrogen) and 16 (the mass of oxygen) until you come up with sensible fragment ions.

Other ions are matched to the peaks here:



Tip: Only the ions show up on the mass spectrum — the free radicals are 'lost' because they are uncharged.

Tip: Being able to analyse and interpret the mass spectrum of a molecule is a vital part of organic chemistry. It's an important technique used by research scientists for identifying unknown compounds or confirming the identity of a product in organic synthesis.

Tip: The little numbers above the peaks here are their exact *m/z* values.

Fragment	*m/z*
CH_3^+	15
$CH_3CH_2^+$	29
$CH_3CH_2CH_2^+$ or $CH_3CHCH_3^+$	43
OH^+	17
$C{=}O^+$	28
$COCH_3^+$	43

Figure 2: *Common fragment ions.*

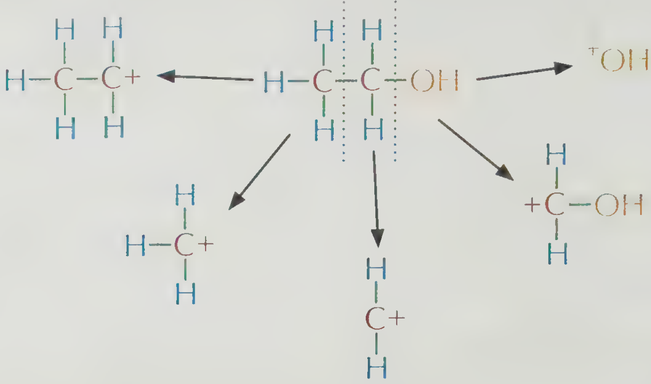
Exam Tip

You won't be given a common fragments table in the exam. But don't worry — if you can't remember an *m/z* value, you can work it out by finding the M_r of the ion For example: $OH^+ = 16 + 1 = 17$.

Exam Tip
Getting your head around these mass spectra is always difficult at first — get loads of practice in before the exam and you'll soon pick it up.

Exam Tip
Don't worry if you can't assign every line to a fragment — just make sure you assign most of them and that your final molecule makes sense.

The next step is piecing them together to form a molecule with the correct M_r. Ethanol has all the fragments on this spectrum.



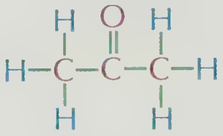
Ethanol's formula is C_2H_6O, and its molecular mass is 46 — the same as the *m/z* value of the M peak. So, this is the mass spectrum of ethanol.

Differentiating between similar molecules

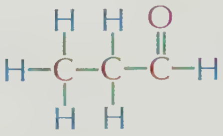
Even if two different compounds contain the same atoms, you can still tell them apart with mass spectrometry because they won't produce exactly the same set of fragments.

Example

The formulas of propanone and propanal are shown below.



propanone

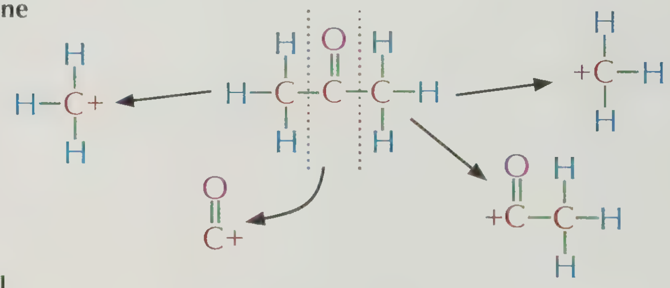


propanal

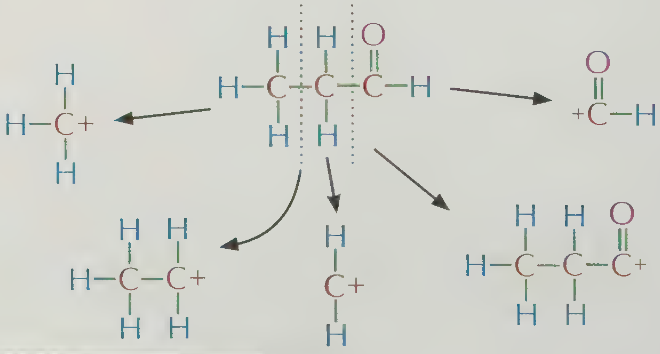
They've got the same M_r, but different structures, so they produce some different fragments.

Tip: For example, the mass spectrum of propanone will have a peak an *m/z* of 43 (thanks to the CH_3CO^+ ion), but the spectrum of propanal won't. And the mass spectrum of propanal will have a peak at an *m/z* of 29 (because of the $CH_3CH_2^+$ ion and the CHO^+ ion), but the spectrum of propanone won't.

Propanone



Propanal

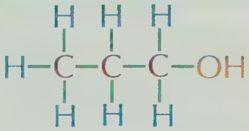


Tip: The fragmentation diagrams on the right don't show all the possible fragments — just some of the main ones.

Every compound produces a different mass spectrum — so the spectrum's like a fingerprint for the compound. Large computer databases of mass spectra can be used to identify a compound from its spectrum.

Practice Questions — Application

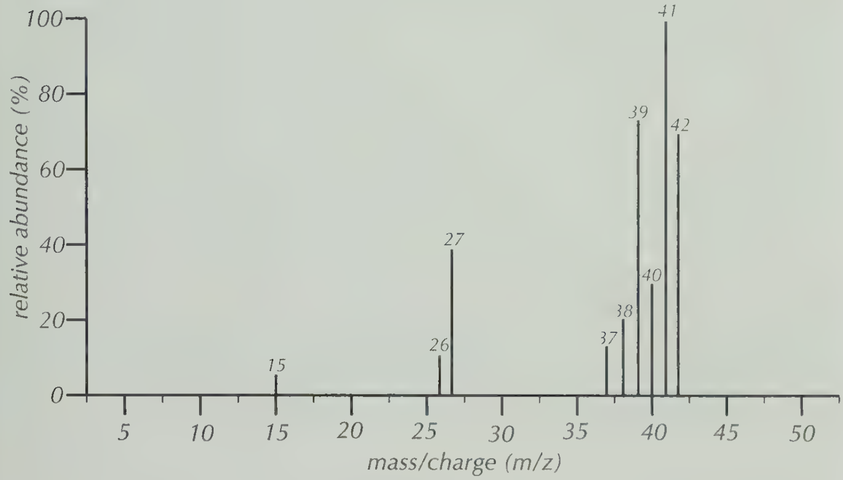
Q1 Write down three possible fragment ions of propan-1-ol. The structure of propan-1-ol is shown on the right.



$\mathrm{H{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}OH}$

Q2 Use the mass spectrum below to work out the structure of the molecule. HINT: The molecule is an alkene.

Tip: You can use Figure 2 on page 273 to help with this question if you like.



Q3 Identify a fragment ion that will appear in the mass spectrum of butan-2-ol but won't appear in the mass spectrum of butan-1-ol.

Tip: If you're struggling to work out what fragments a molecule might produce, draw it out. You'll find it's so much easier to divide the molecule up into fragments when you can see all the atoms and bonds.

Practice Questions — Fact Recall

Q1 What do the *x*-axis and the *y*-axis on a mass spectrum tell you?

Q2 What information does the *m*/*z* value of the M peak give you?

Q3 If you have a peak at an *m*/*z* of 15, what is the most likely fragment ion of an organic compound that it will correspond to?

3. Combined Techniques

Often, it can help to use more than one analytical technique to work out what an organic compound is. Before you start this topic, make sure you're confident working out the formula of a compound from its percentage composition, and you understand how to interpret IR and mass spectra.

Learning Objective:

- Be able to deduce the structures of organic compounds from different analytical data including elemental analysis, mass spectra and IR spectra.

Specification Reference 4.2.4

Identifying compounds

In the exam, you may be asked to identify a compound from a combination of its mass or percentage composition, IR spectrum and mass spectrum.
You may have to do some of the following steps:

1. Use the composition to work out the empirical formula of the compound.
2. Use the mass spectrum to work out the molecular mass of the compound, and use this along with the empirical formula to work out its molecular formula.
3. Work out what functional groups are in the compound from its infrared spectrum.
4. Use the mass spectrum to work out the structure of the molecule using the fragmentation pattern.

Exam Tip
If you're asked to use a variety of methods to identify a compound, make sure you refer to all the sources of data in your answer. So if you're asked to identify a compound using a mass spectrum and an IR spectrum, make sure you write about what both the spectra show you, even if you can figure it out from just one of them.

Example — **Maths Skills**

An unknown organic compound has a percentage composition of C: 62.1%, H: 10.3%, O: 27.6%. The mass spectrum of the compound is shown in Figure 1, and the infrared spectrum is shown in Figure 2.
Suggest a structure for the unknown compound.

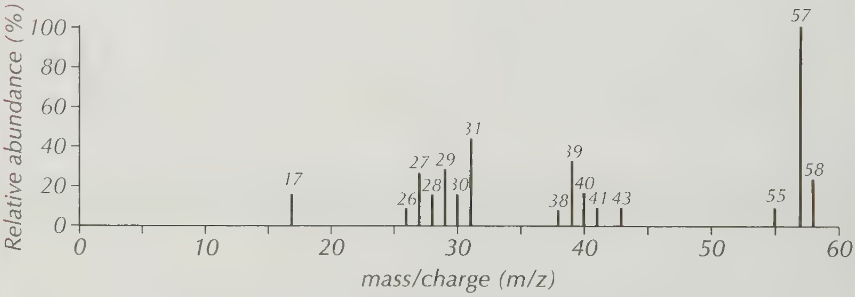


Figure 1: *The mass spectrum of an organic compound.*

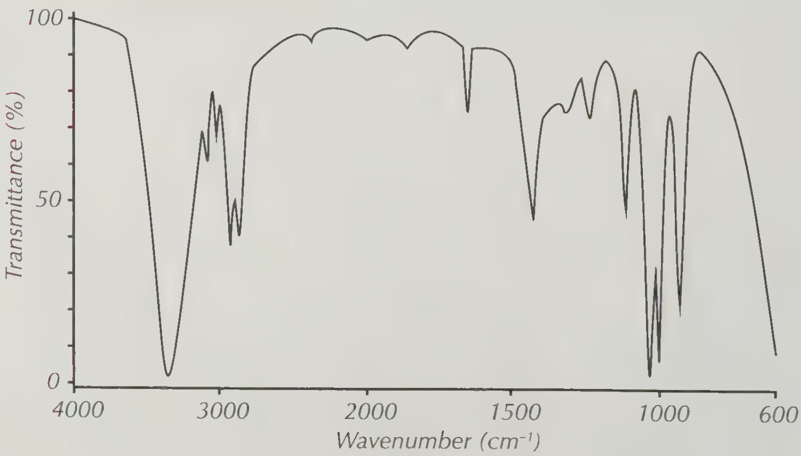


Figure 2: *The infrared spectrum of an organic compound.*

Tip: Being able to predict what a compound is from one type of analytical technique is fine, but if you get the same answer using more than one technique as evidence then you can be more confident of your answer.

HOW SCIENCE WORKS

First, work out the empirical formula using the percentage composition of the compound:

- If you had 100 g of the compound, there would be 62.1 g of carbon, 10.3 g of hydrogen and 27.6 g of oxygen.
  Using the formula moles = mass ÷ M_r, you can work out how many moles of each element that is:
  C: $\frac{62.1}{12} = 5.18$ mol H: $\frac{10.3}{1} = 10.3$ mol O: $\frac{27.6}{16} = 1.73$ mol
- Divide each number of moles by the smallest number (here it's 1.73):
  C: $\frac{5.18}{1.73} \approx 3$ H: $\frac{10.3}{1.73} \approx 6$ O: $\frac{1.73}{1.73} = 1$
- This tells you that the ratio of the elements C : H : O in the compound is 3 : 6 : 1. So the empirical formula is **C_3H_6O**.

Tip: There's more about calculating the formula of a compound from its percentage composition on pages 63-64.

Next, use the mass spectrum to find the molecular mass of the compound:

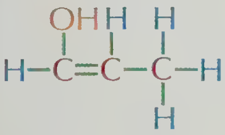
- The peak with the highest mass (the M peak) in Figure 1 has an *m*/*z* of 58, so the molecular mass of the compound is 58.
- The empirical formula has $M_r = (3 \times 12) + (6 \times 1) + (1 \times 16) = 58$. Since the empirical mass is the same as the molecular mass of the compound, the molecular formula will be **C_3H_6O**.

The easiest way to identify the functional groups in the molecule is by looking at the IR spectrum.

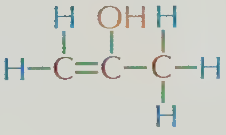
- The spectrum shows a peak at about 3200 cm^{-1}, which is likely to be due to an -OH group.
- There is also a peak at about 3000 cm^{-1} due to the vibrations of the C–H bonds and a peak at about 1650 cm^{-1}, which is likely to be due to vibrations of C=C bonds. These peaks imply that the molecule is an **alcohol** and also has an **alkene** group.

Tip: The molecule must be an alcohol or a carbonyl — it can't be a carboxylic acid as there's only one oxygen atom in the molecular formula.

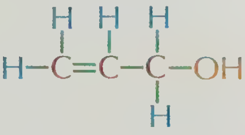
You can now start piecing together the information to draw some potential structures for your compound. The following structural isomers all have a hydroxyl group, an alkene group and a molecular formula of C_3H_6O:



1-propen-1-ol



1-propen-2-ol



2-propen-1-ol

Tip: Look back at pages 211-212 for the rules on how to name organic molecules.

Now it's time to go back to the mass spectrum to identify what fragments are in the molecule:

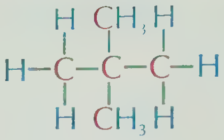
- The peak at *m*/*z* = 31 is likely to be a CH_2OH^+ fragment.
- The peak at *m*/*z* = 27 is likely to be a CH_2CH^+ fragment.
- The spectrum doesn't have a peak at *m*/*z* = 15, so it's unlikely that there's a CH_3 fragment in the molecule.

The spectrum shows that the compound must be **2-propen-1-ol**, as this is the only isomer that has a CH_2OH fragment, a CH_2CH fragment and no CH_3 fragment.

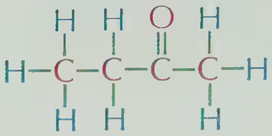
Practice Questions — Application

Q1 Explain which of the compounds A, B or C is represented by the data below:

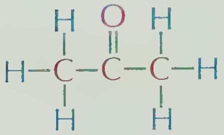
A



B

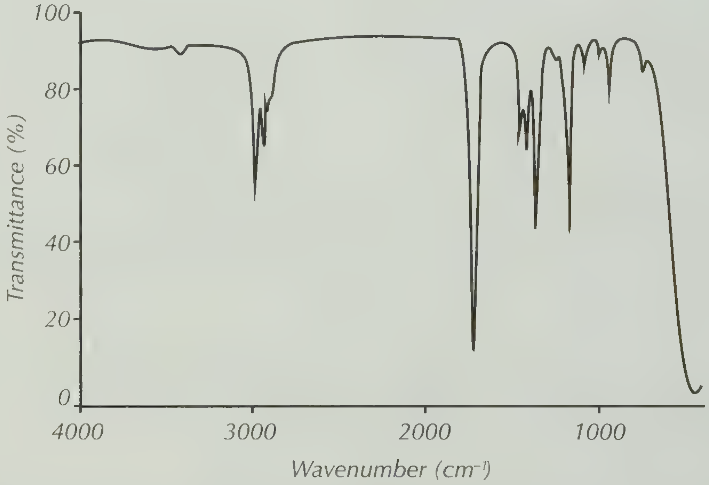


C



The mass spectrum of the compound has a molecular ion peak at an *m*/*z* of 72.

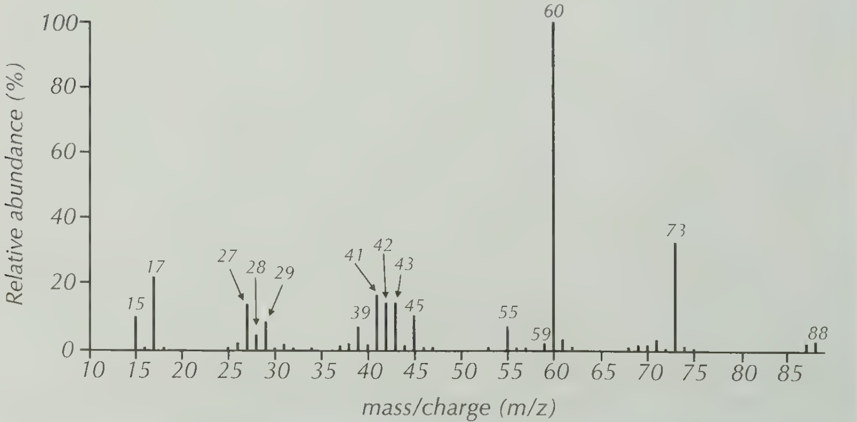
The infrared spectrum of the compound is:



Tip: Don't get confused between IR spectroscopy and mass spectrometry. Remember — if you're given an IR spectrum, you want to be looking at the functional groups in a molecule. But if you're given a mass spectrum, you need to look at the structure and what fragments you're likely to get.

Tip: Use the table on page 267 to help identify the IR peaks.

Q2 An organic compound that can be made by oxidising a primary alcohol has percentage composition: C: 54.5%, H: 9.01%, O: 36.4%. Its mass spectrum is shown below.
Predict, with reasoning, the identity of the organic compound.



Tip: Remember that you don't have to assign every peak to a fragment in a mass spectrum.

4. Practical Techniques in Organic Synthesis

PRACTICAL ACTIVITY GROUP 5

There are some practical techniques that get used a lot in organic chemistry. They may be used during the synthesis of a product, or to purify it from unwanted by-products or unreacted reagents once it's been made.

Learning Objectives:

- Be able to describe and use the techniques and procedures for the use of Quickfit apparatus, including for distillation and heating under reflux (PAG 5).
- Be able to describe and use the techniques and procedures for the preparation and purification of an organic liquid, including how to use a separating funnel to remove an organic layer from an aqueous layer, how to dry an organic layer with an anhydrous salt (e.g. $MgSO_4$, $CaCl_2$), and redistillation (PAG 5).

Specification Reference 4.2.3

Reflux

Organic reactions are slow and the substances are usually flammable and volatile (they've got low boiling points). If you stick the reactants in a beaker and heat them with a Bunsen burner they'll evaporate or catch fire before they have time to react. You can **reflux** a reaction to get round this problem.

When you carry out a reaction under reflux, the mixture's heated in a flask fitted with a vertical **Liebig condenser**. This means the mixture can be continuously boiled, and as the vapours evaporate into the condenser they condense and are recycled back into the flask, giving them time to react.

The heating is usually electrical — hotplates, heating mantles or electrically controlled water baths are normally used. This avoids naked flames that might ignite the compounds.

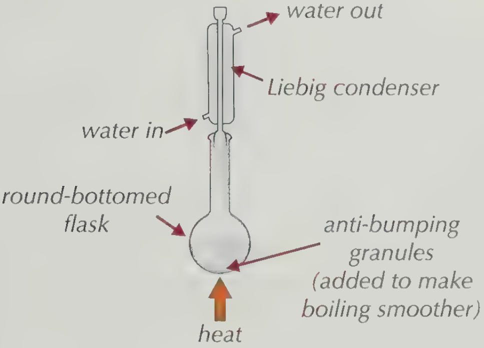


Figure 1: *Reflux apparatus.*

Tip: The chemicals you use in organic reactions are often hazardous. You should always carry out a full risk assessment before you do any reactions in the lab.

Example

The reaction between butan-2-ol and acidified potassium dichromate(VI) to make butanone is slow at room temperature, so it needs to be heated.

Butanone has a boiling point of 80 °C and butan-2-ol has a boiling point of about 100 °C, so if you were to heat the reaction in a beaker then lots of the reactant and product compounds would evaporate out of the mixture and be lost.

By heating the reaction under reflux, the rate of the reaction is increased but neither the starting materials nor the product can evaporate out of the apparatus, so the yield isn't reduced.

Distillation

Distillation separates liquids with different boiling points. It works by gently heating a mixture in a distillation apparatus. The substances will evaporate out of the mixture in order of increasing boiling point.

Figure 2: *Two students carrying out a reflux reaction.*

A thermometer is placed at the neck of the condenser and shows the boiling point of the substance that is evaporating at any given time. If you know the boiling point of your pure product, you can use the thermometer to tell you when it's evaporating and therefore when it's condensing.

If the product of a reaction has a lower boiling point than the starting materials, then the reaction mixture can be heated in a distillation apparatus so that the product evaporates from the reaction mixture as it forms. As long as the temperature is controlled, the starting materials won't evaporate from the reaction mixture.

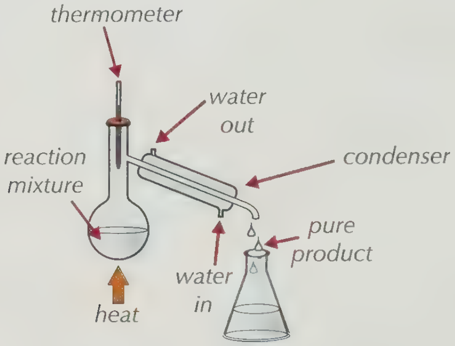


Figure 3: *Distillation apparatus.*

Tip: Secondary alcohols are oxidised to ketones by acidified potassium dichromate(VI) solution. Primary alcohols are oxidised first to aldehydes and then to carboxylic acids. There's more on this on pages 251-252.

Example

Hexan-1-ol reacts with acidified dichromate(VI) solution to form hexanal. However, hexanal can be further oxidised by acidified dichromate(VI) to form hexanoic acid.

By heating the reaction in a distillation apparatus at a temperature of around 131 °C (the boiling point of hexanal), any hexanal that is produced will immediately evaporate out of the reaction mixture. Hexan-1-ol, which has a boiling point of about 155 °C, won't evaporate, so stays in the reaction mixture and can react fully to form hexanal. The hexanal that is distilled out of the reaction mixture can be collected in a separate vessel. This prevents it from being oxidised further to hexanoic acid.

Redistillation

Mixtures that contain volatile liquids can be purified using a technique called **redistillation**. If a product and its impurities have different boiling points, then redistillation can be used to separate them. You just use the same distillation apparatus as shown above, but this time you're heating an impure product, instead of the reaction mixture.

When the liquid you want boils (this is when the thermometer is at the boiling point of the liquid), you place a flask at the open end of the condenser ready to collect your product. When the thermometer shows the temperature is changing, put another flask at the end of the condenser because a different liquid is about to be delivered.

Tip: Water-soluble impurities might include salts (such as NaCl) or short-chain organic compounds that are capable of forming hydrogen bonds (such as alcohols, carbonyls and carboxylic acids).

Separation

If the product is insoluble in water then you can use a separating funnel to remove any impurities that do dissolve in water, such as salts or water-soluble organic compounds (e.g. alcohols).

Once the reaction is completed, the mixture is poured into the separating funnel, and water is added. The funnel is shaken and then allowed to settle (see Figure 4). The organic layer is normally less dense than the aqueous layer, so should float on top. Most of the water-soluble impurities should have dissolved in the lower aqueous layer. You can then open the stopper on the separating funnel, run off the aqueous layer and collect your product.

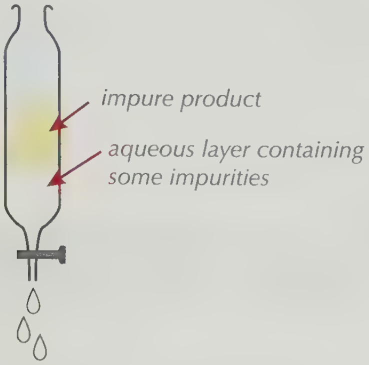


Figure 4: *Separating apparatus.*

Tip: Your product won't necessarily be pure after separation — any organic impurities that don't dissolve in water will still be in the organic layer alongside your product. You'll probably need to remove them by redistillation. There may also be a few water soluble impurities left in the organic layer. To get rid of these, you'll need to repeat the separation.

Figure 5: *A student using a separating funnel to separate an organic and an aqueous layer.*

Drying agents

If you use separation to purify a product, the organic layer will end up containing trace amounts of water, so it has to be dried. To do this you can add an anhydrous salt such as magnesium sulfate ($MgSO_4$) or calcium chloride ($CaCl_2$). The salt is used as a **drying agent** — it binds to any water present to become hydrated. The drying agent will become lumpy when you first add it to the organic layer — this means you need to add more. You know that all the water has been removed when you can swirl the mixture and it looks like a snow globe. The mixture, which may have looked cloudy due to the presence of tiny water droplets at the beginning, should also go clear when it's dry and the drying agent has settled to the bottom. You can filter the mixture to remove the solid drying agent.

Tip: If you're asked about how you could go about separating a mixture, you need to think about the properties of the different compounds. For example, hexane is insoluble in water and has a boiling point of 68 °C. Ethanol is soluble in water and has a boiling point of 78 °C.

Practice Questions — Application

Q1 Suggest how you could separate a mixture of hexane and ethanol into its component parts.

Q2 Jomei wants to make the compound 4-hydroxypentan-2-one by heating pentane-2,4-diol with acidified potassium dichromate(VI). If the reaction is left for too long, the starting material ends up being oxidised twice to form a compound with two carbonyl groups. Suggest a method Jomei could use to prevent the starting material from being over-oxidised.

Practice Questions — Fact Recall

Q1 Draw a labelled diagram of the apparatus used to reflux a reaction.

Q2 What physical property is used to separate compounds in redistillation?

Q3 Name two compounds that can be used as drying agents.

Exam Tip
Always remember to label diagrams if you have to draw them in the exam.

5. Organic Synthesis

Learning Objectives:

- Be able to identify individual functional groups and predict the properties and reactions of an organic molecule containing several functional groups.
- Be able to design two-stage synthetic routes for preparing organic compounds.

Specification Reference 4.2.3

In the exam, you might have to explain how you could synthesise one compound from another, so here's a summary of all the homologous series and reactions you've met so far. It might look like a lot of information, but don't panic — you've seen most of it before.

Typical reactions of functional groups

The different properties of functional groups influence their reactivity — for example, nucleophiles don't react with the electron-rich double bond in alkenes, but they do attack the δ+ carbon in haloalkanes. Figure 1 is a summary of all the functional groups you've studied so far, along with how to name them and how they'll typically react:

Homologous series	Functional group	Prefix/ suffix	Properties	Typical reactions
Alkane	only C–C and C–H	-ane	Non-polar, unreactive	Radical substitution
Alkene	C=C	-ene	Non-polar, electron-rich double bond	Electrophilic addition
Alcohol	C–OH	-ol (or hydroxy-)	Polar C–OH bond	Nucleophilic substitution/ Dehydration/ Elimination/Oxidation
Haloalkane	C–X	halo- (e.g. chloro-)	Polar C–X bond	Nucleophilic substitution
Ketone	C=O	-one	Polar C=O bond	—
Aldehyde	HC=O	-al	Polar C=O bond	Oxidation
Carboxylic acid	-COOH	-oic acid	Electron-deficient carbon centre	—

Figure 1: *The homologous series and organic reactions in Module 4.*

Tip: Now you've learnt about lots of organic reactions, you can use them to work out how you could make one compound from another. That's what organic chemistry's all about.

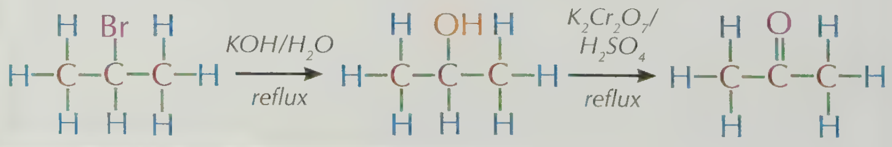
HOW SCIENCE WORKS

Synthetic Routes

Chemists need to be able to make one compound from another. It's vital for things such as designing medicines. It's not always possible to synthesise a desired product from a starting material in just one reaction. A synthetic route shows how you get from one compound to another. It shows all the reactions with the intermediate products, and the reagents needed for each reaction.

Example

You can't produce propanone from 2-bromopropane via one reaction. Instead you first have to make propan-2-ol. The synthetic route is:



Here are all the organic reactions you've met so far:

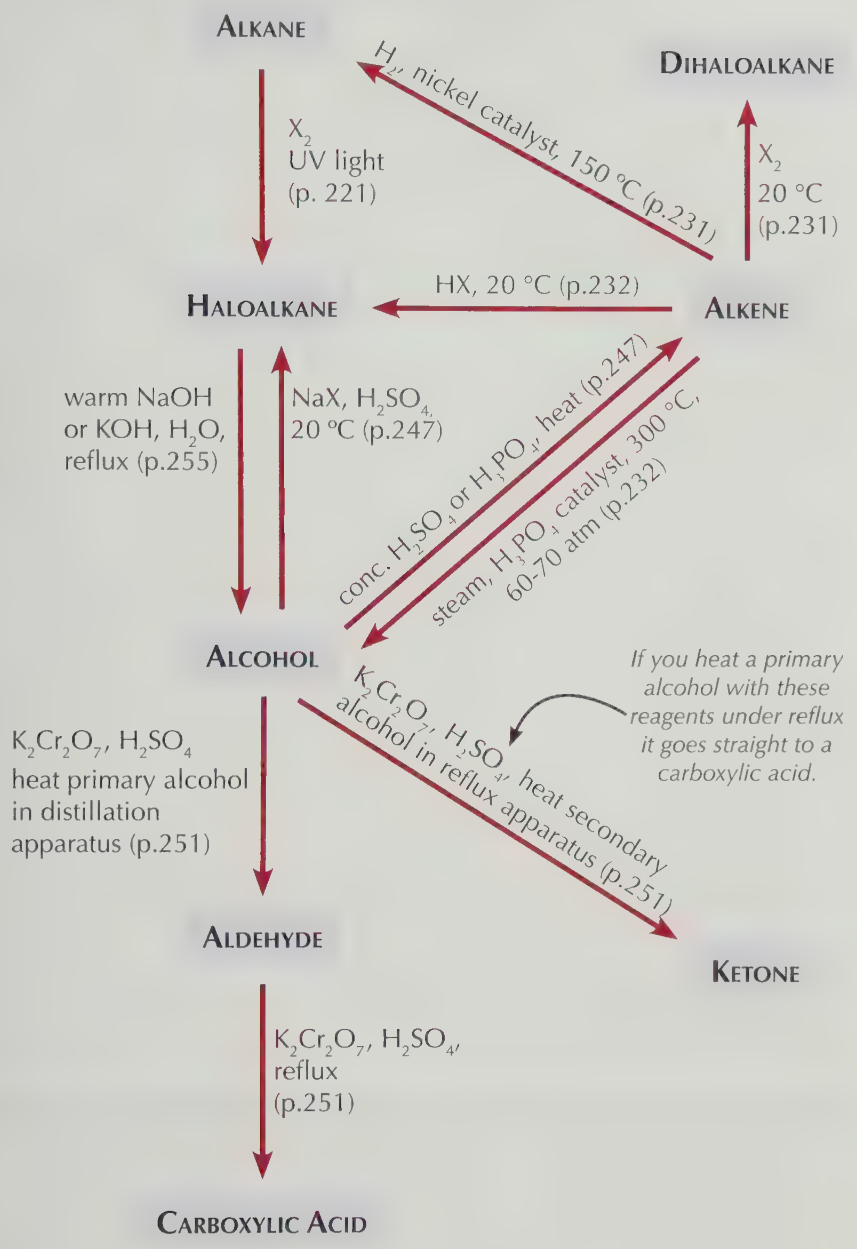

ALKANE
DIHALOALKANE
HALOALKANE
ALKENE
ALCOHOL
ALDEHYDE
KETONE
CARBOXYLIC ACID
X_2 UV light (p. 221)
H_2, nickel catalyst, 150 °C (p.231)
X_2 20 °C (p.231)
HX, 20 °C (p.232)
warm NaOH or KOH, H_2O, reflux (p.255)
NaX, H_2SO_4, 20 °C (p.247)
conc. H_2SO_4 or H_3PO_4, heat (p.247)
steam, H_3PO_4 catalyst, 300 °C, 60-70 atm (p.232)
$K_2Cr_2O_7$, H_2SO_4 heat primary alcohol in distillation apparatus (p.251)
$K_2Cr_2O_7$, H_2SO_4, heat secondary alcohol in reflux apparatus (p.251)
If you heat a primary alcohol with these reagents under reflux it goes straight to a carboxylic acid.
$K_2Cr_2O_7$, H_2SO_4, reflux (p.251)

Figure 2: *A summary of organic reactions that could be used in synthetic routes.*

If you're asked how to make one compound from another in the exam, make sure you include:

- Any special procedures, such as refluxing.
- The conditions needed, e.g. high temperature or pressure, or the presence of a catalyst.

Tip: The reaction between an alkene and a halogen to form a dihaloalkane using bromine water ($Br_{2\,(aq)}$) can be used as a test for unsaturation (see page 232).

Tip: To form an alcohol from a haloalkane, you could also use H_2O in the presence of $AgNO_3$. This reaction is used to test the strength of different carbon-halogen bonds (see page 256).

Tip: If it says a reaction is carried out at 20 °C, it just means it's done at room temperature.

Tip: Remember — aldehydes form from primary alcohols and ketones from secondary alcohols.

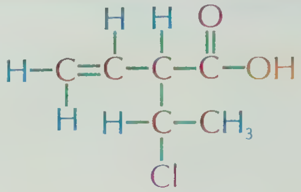
Tip: Hydrocarbons (organic molecules that contain only hydrogen and carbon) also combust in oxygen to form carbon dioxide and water (page 217).

Tip: When you're planning a synthetic route, you should aim to get from the first compound to the last in as few steps as possible.

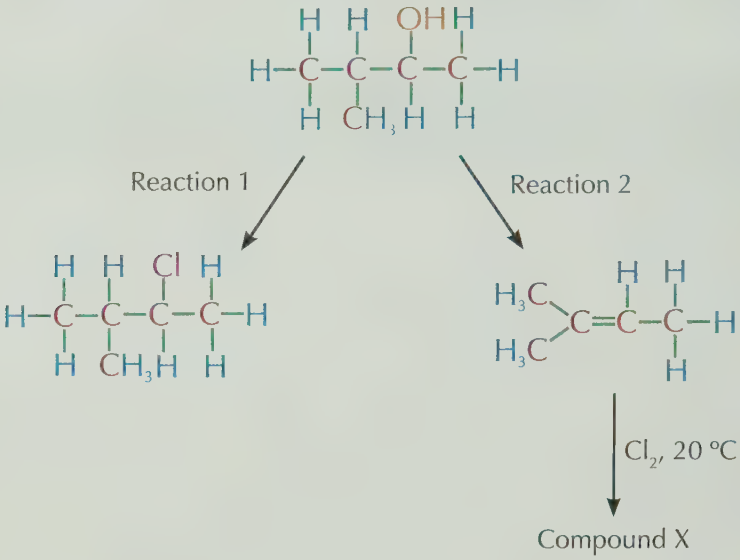
Tip: The summary diagram on page 283 will be really useful for these questions.

Practice Questions — Application

Q1 Name all the functional groups in the following molecule:



Q2 The diagram below shows how some haloalkanes can be produced from an alcohol:



a) What reagents and conditions are needed in Reaction 1?

b) What reagents and conditions are needed in Reaction 2?

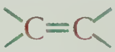
c) Draw the structure of Compound X.

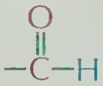
Q3 Devise a two-stage synthetic route that could be used to produce pentanoic acid from 1-bromopentane.

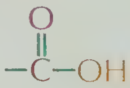
Exam Tip
If a question asks for a synthetic route, remember to give all the special procedures, conditions and reagents you need. Missing out any could cost you valuable marks...

Practice Questions — Fact Recall

Q1 Name the homologous series that contain the following functional groups:

a) 

b) 

c) 

Q2 Give one of the typical reactions of the following compounds:

a) a haloalkane

b) an alkane

c) an alcohol

Q3 What conditions and reagents are required to synthesise an alkane from an alkene?

Q4 What would happen if you heated a primary alcohol under reflux with potassium dichromate(VI) in acidic conditions?

Section Summary

Make sure you know...

- That absorption of infrared radiation causes covalent bonds to vibrate.
- How to identify an alcohol, an aldehyde, a ketone and a carboxylic acid from the absorption peaks in an infrared spectrum.
- How to interpret and predict the infrared spectra of unfamiliar molecules.
- That modern breathalysers measure ethanol in the breath using infrared spectroscopy.
- That gases causing air pollution, such as CO and NO, can be monitored using infrared spectroscopy.
- How to use the molecular ion peak on a mass spectrum to determine the molecular mass of a molecule.
- How to use the fragmentation pattern of a mass spectrum to identify the structure of a molecule.
- How to use a combination of analysis techniques, such as elemental analysis, infrared spectra and mass spectra, in order to deduce the structures of organic compounds.
- How to prepare an organic liquid by heating under reflux and by distillation.
- How to purify an organic liquid by redistillation.
- That you can purify an organic liquid by using a separating funnel to remove aqueous impurities.
- How to use anhydrous salts, such as anhydrous $MgSO_4$ or anhydrous $CaCl_2$, to dry organic liquids.
- The different functional groups in an organic molecule and how to identify them.
- How to predict the properties and reactions of an organic molecule based on its functional groups.
- How to devise a two-stage synthetic route to prepare an organic compound.

Exam-style Questions

1 Identify which of the steps in the following method for purifying an organic compound that is immiscible with water from water-soluble impurities is incorrect:

A Pour the organic mixture into a separating funnel and add water.

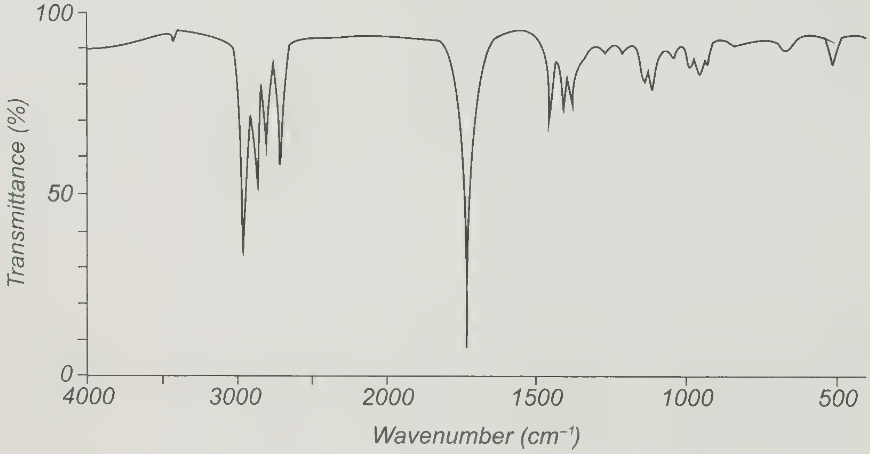
B Put a stopper in the separating funnel and shake it. Remove the stopper and allow the layers to settle.

C Run out the lower, aqueous, layer and discard it.

D Run out the upper, organic, layer and dry it with hydrated magnesium sulfate.

(1 mark)

2 Predict which compound is represented by the infrared spectrum shown below.



A butanol

B butanal

C butanoic acid

D butene

(1 mark)

3 Which of the following is not a valid one-stage synthetic route?

A alcohol → carboxylic acid

B dihaloalkane → haloalkane

C alcohol → alkene

D alkene → alkane

(1 mark)

4 A student synthesises the alcohol hexan-3-ol from an alkene in a one-stage synthesis.

(a) Name an alkene that could be used as the starting material for synthesising hexan-3-ol.

(1 mark)

(b) Give the reagents and conditions needed to synthesise hexan-3-ol from an alkene.

(2 marks)

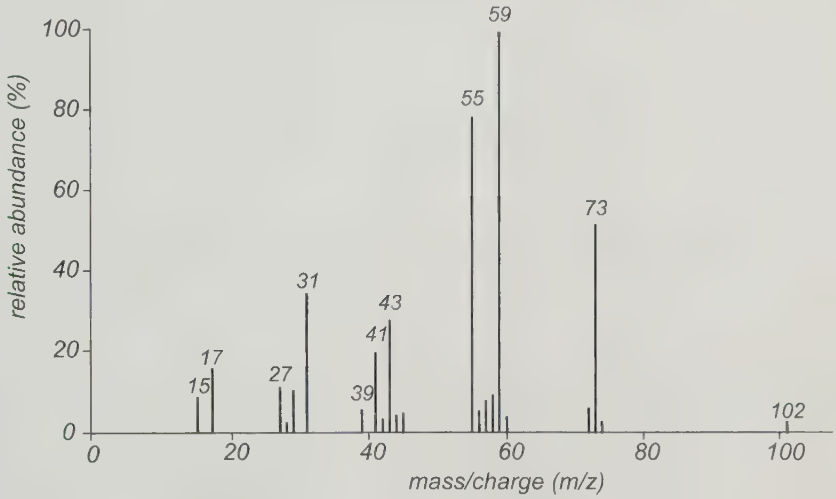
(c) Give one difference that you would expect to see between the infrared spectra of the starting alkene and hexan-3-ol.

(1 mark)

(d) The student purifies her product by redistillation.
Draw a labelled diagram of the apparatus used in redistillation.

(3 marks)

(e) Once the student has carried out her reaction, she records a mass spectrum of the purified product, shown below. Use the spectrum to confirm whether hexan-3-ol was successfully synthesised. Explain your answer.



(3 marks)

5 1,2-dichloroethane is an organic molecule, used in part of the manufacturing process of the polymer PVC.

(a) Describe a synthetic route which could be used to successfully produce 1,2-dichloroethane from ethanol. You should include details of any reaction conditions, reagents and intermediates formed in your synthetic route.

(4 marks)

(b) A student successfully synthesises 1,2-dichloroethane from ethanol, but finds her product contains trace amounts of unreacted ethanol. Suggest a technique the student could use to purify her product.

(1 mark)

6 Mass spectrometry and infrared spectrometry are two analytical techniques that are used to identify unknown compounds.

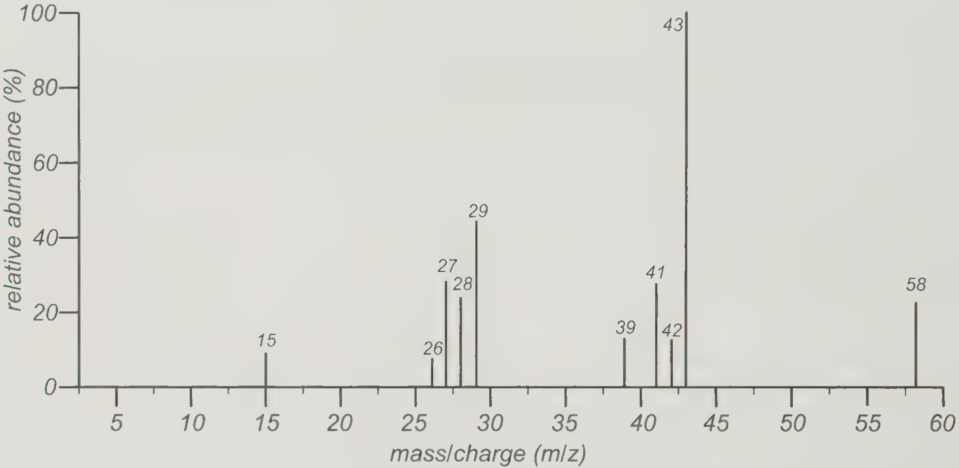
(a) Describe how infrared spectroscopy can help to catch drunk drivers.

(2 marks)

(b) Briefly outline why mass spectrometry can be used to differentiate between similar molecules.

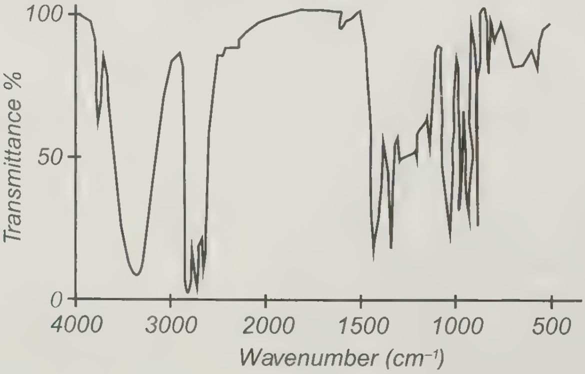
(1 mark)

(c) Molecule **J** is a hydrocarbon. The mass spectrum of molecule **J** is shown below. Identify the structure of molecule **J**. Explain your reasoning.



(4 marks)

(d) Molecule **K** contains only carbon, oxygen and hydrogen atoms. It has the infrared spectrum shown below.



The mass spectrum of molecule **K** shows that the M_r of the molecule is 74.

If you react molecule **K** with acidified potassium dichromate(VI), you produce a ketone.

Use your knowledge of organic chemistry and analytical techniques along with the table on page 267 to identify the structure of molecule **K**. Explain your reasoning.

(4 marks)

Module 5 Section 1: Reaction Rates

1. Monitoring Reactions

Understanding all about the rates of chemical reactions is a really important part of A Level Chemistry. You've already encountered reaction rates in Module 3: Section 2, but now it's time to cover things in a bit more detail.

Learning Objectives:

- Be able to explain and use the term rate of reaction.
- Understand the techniques and procedures used to investigate reaction rates by continuous monitoring, including use of colorimetry (PAG 9).

Specification Reference 5.1.1

What are reaction rates?

The **reaction rate** is the change in the amount of reactants or products per unit time (normally per second). For example, if the reactants are in solution, the rate will be the change in concentration per second — the units will be mol dm^{-3} s^{-1}.

Continuous monitoring

PRACTICAL ACTIVITY GROUP 9

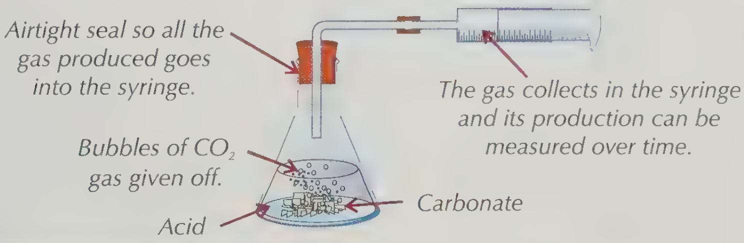
You might want to know how the rate of a reaction changes during the course of a reaction. One way of doing this is to measure how the amount of a product or reactant changes over the complete course of the reaction. This is called **continuous monitoring**. There are quite a few ways to follow reactions, but not every method works for every reaction. You've got to study a property that changes as the reaction goes on. Here are a few examples:

Measuring the formation of a gas

If a gas is given off, you could collect it in a gas syringe and record how much you've got at regular time intervals.

Example

This would work for the reaction between an acid and a carbonate in which carbon dioxide gas is given off.

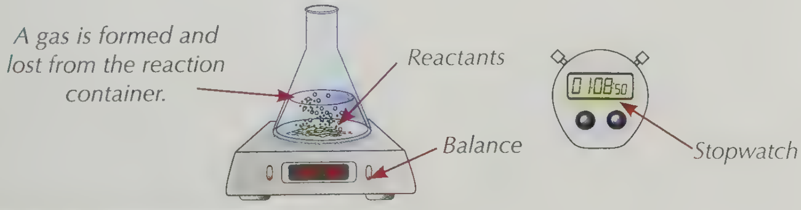

Airtight seal so all the gas produced goes into the syringe.
The gas collects in the syringe and its production can be measured over time.
Bubbles of CO_2 gas given off.
Carbonate
Acid

Tip: As well as continuous monitoring, you can also measure the rate of a reaction using a technique called the 'initial rates method'. See pages 295-296 for more on this.

You could also measure the change in mass of the reaction vessel at regular intervals as the gas is lost, using a mass balance.

Example

The reaction between sodium hydrogen carbonate and an acid can be monitored by measuring the mass lost as carbon dioxide gas is evolved:


A gas is formed and lost from the reaction container.
Reactants
Balance
0 108 50
Stopwatch

Tip: Both of these methods for monitoring the formation of a gas have already been covered in more detail, so have a look back at pages 185-186 for more information.

Figure 1: A student using a colorimeter as part of a colorimetry experiment. A digital display shows the absorbance value of a sample at any given moment.

Measuring a colour change

Sometimes you can track a colour change of a reaction using a gadget called a colorimeter. Colorimeters measure the absorbance of a particular wavelength of light by a solution. If they're set to measure the absorbance of a wavelength that is absorbed by one of the reactants but not by the products (or vice versa), then the change in absorbance over the course of the reaction can be used to measure the rate. Here's how you use a colorimeter:

- First, set the colorimeter to measure the wavelength of light that you're interested in measuring.
- Next, calibrate the colorimeter. Place a sample of distilled water in a sample tube, known as a cuvette, and place it in the colorimeter. Set the absorbance to zero.
- Carry out your reaction. You should take samples from the reaction mixture at regular intervals, and measure the absorbance of each one using the colorimeter.

Tip: Before you carry out any of these techniques for monitoring the progress of a reaction, make sure you do a risk assessment.

Example

You could monitor the reaction between propanone and iodine using colorimetry. As the reaction progresses, the brown colour fades.

$$\underset{\text{colourless}}{CH_3COCH_{3\,(aq)}} + \underset{\text{brown}}{I_{2\,(aq)}} \rightarrow \underbrace{CH_3COCH_2I_{(aq)} + H^+_{(aq)} + I^-_{(aq)}}_{\text{colourless}}$$

Measuring a change in pH

If either hydrogen or hydroxide ions are produced or used up in a reaction, then you can monitor the progress of the reaction by measuring the change in the pH.

Tip: You can measure the pH of a mixture using a pH meter.

Example

In the reaction between propanone and iodine above, H^+ ions are produced, so you can monitor the progress of the reaction by measuring the change in pH.

Processing data

Once you've carried out your experiment, you may want to draw a concentration-time graph of your results to work out more information about the reaction and its rate. To do this, you may first have to process your data to get it into units of concentration. Here are some examples to show you how it's done.

Tip: You don't always monitor the amount of product produced — sometimes it's easier to monitor the consumption of a reactant instead.

Examples

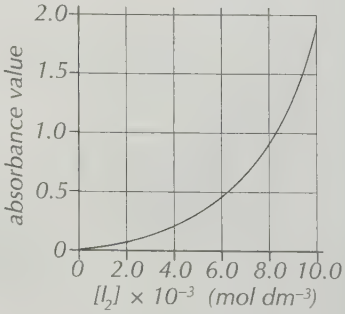
Colorimetry

A student follows the rate of the following reaction by measuring the change in absorbance of a wavelength of light that is absorbed by I_2:

$$CH_3COCH_3 + I_2 \rightarrow CH_3COCH_2I + H^+ + I^-$$

For each data point, the student will have to convert the absorbance reading into a concentration of I_2. He can do this using a calibration curve for the absorbance of a wavelength of light by solutions of different concentrations of I_2.

So, if at any point the absorbance of the reaction solution was 1.3, the concentration of I_2 was **9.0×10^{-3} mol dm^{-3}**.



Tip: To plot a calibration curve like the one on the right, you'll need to measure the absorbances of some standard solutions of I_2 of various concentrations.

pH

A student follows the rate of the following reaction by measuring the change in pH:

$$NaHCO_3 + HCl \rightarrow NaCl + H_2O + CO_2$$

For each data point, the student will have to convert the pH into a concentration in order to plot a concentration-time graph for HCl. She can do this by rearranging the equation:

$$pH = -\log[H^+] \text{ to } [H^+] = 10^{-pH}.$$

Since HCl is a strong, monobasic acid, the concentration of H^+ is equal to the concentration of HCl.

So if, for example, after 20 seconds the pH was 5.20, the concentration of H^+ ions (and therefore the concentration of HCl) would be:

$$10^{-5.20} = \mathbf{0.0000063\ mol\ dm^{-3}}$$

Tip: Don't worry if all this pH stuff looks unfamiliar. There's loads more about calculating the concentration of H^+ ions or OH^- ions in solution from the pH on pages 341 and 345.

If you've measured the formation of a product, but you want to draw a concentration-time graph to follow one of the reactants to, for example, work out the reaction order (see page 301), then you'll have to carry out the following steps for each of your data points:

- Use the initial concentration of the reactant you're interested in to work out how many moles of it there were at the start of the reaction.
- For each data point, work out how many moles of product have formed (how you do this will vary, depending on what the experimental data is).
- Use the balanced reaction equation to work out how many moles of the reactant you're interested in have been used.
- Subtract the number of moles of reactant used from the initial number of moles of the reactant to find the number of moles of reactant at that time point.
- Divide the number of moles of that reactant by the volume of the reaction mixture to find the concentration of the reactant at that time.

Tip: Doing this sort of data processing can take an absolute age if you do it all by hand, and there's lots of potential for making mistakes. Using computer software, such as Microsoft Excel®, can make the whole process much quicker and less painful.

Example

A student follows the rate of the following reaction by measuring the volume of carbon dioxide gas evolved over time:

$$NaHCO_{3(s)} + HCl_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(l)} + CO_{2\,(g)}$$

The reaction mixture starts with 25.0 cm^3 of 1.50 mol dm^{-3} HCl, and the reaction takes place at 298 K. After 40 s, 0.490 dm^3 of gas has been evolved.

- The initial concentration of HCl is 1.50 mol dm^{-3}, and the reaction mixture has a volume of 25.0 cm^3.
  So, initial number of moles of HCl = volume × concentration
  = (25.0 ÷ 1000) × 1.50 = 0.0375 moles.
- To find the number of moles of gas evolved after 40 seconds, rearrange the equation $pV = nRT$ to give $n = (pV) \div (RT)$.
  So $n = (1.0 \times 10^5 \times 0.490 \times 10^{-3}) \div (8.31 \times 298) = 0.0197...$ moles
- From the reaction equation, you can see that 1 mole of HCl reacts to form 1 mole of CO_2, so given that after 40 s, 0.0197... mol CO_2 has been produced, 0.0197... moles of HCl will have been used.
- The number of moles left of HCl is 0.0375 – 0.0197... = 0.0177... moles.
  So [HCl] after 40 seconds is 0.0177... ÷ (25.0 ÷ 1000) = **0.709 mol dm^{-3}**.

Tip: The equation $pV = nRT$ is the ideal gas equation. Have a look back at page 52 if your memory of it is a bit fuzzy. Under standard conditions, $p = 1.0 \times 10^5$ Pa, $T = 298$ K and $R = 8.31$ J K^{-1} mol^{-1}. V is the volume in m^3.

Tip: You could also monitor this reaction by measuring the change in mass of the reaction vessel as CO_2 was lost. If this was the case, you'd first have to work out the change in mass of the reaction vessel at each data point. Then, to find the number of moles of CO_2 corresponding to this change in mass, you could use the equation moles = mass ÷ M_r.

Practice Questions — Application

Tip: Think carefully about the reactants and products present in each of these reactions. It may help you to write out a chemical equation.

Q1 Suggest a technique you could use to follow the progress of each of the following reactions.

a) The reaction between chromate(VI) ions (CrO_4^{2-}) and an acid to form dichromate(VI) ions ($Cr_2O_7^{2-}$) and water.

b) The reaction between zinc metal and hydrochloric acid.

c) The reaction between thiosulfate ($S_2O_3^{2-}$) and acid to produce sulfur dioxide gas, water and a yellow precipitate of solid sulfur.

Q2 A student is monitoring the rate of a reaction between an acid and a metal by collecting gas in a gas syringe. How would her calculated rate be affected if there was a leak in the system?

Tip: Don't panic if you're asked to convert multiple experimental data points into concentration data. Just follow the same method for each step and you'll be fine.

Q3 A student is using a balance to monitor the loss of mass over the course of the following reaction between zinc sulfide and 250 cm³ of 1.50 mol dm⁻³ hydrochloric acid.

$$ZnS_{(s)} + 2HCl_{(aq)} \rightarrow ZnCl_{2\,(aq)} + H_2S_{(g)}$$

She records the mass of the reaction vessel at various time intervals. Calculate the concentration of HCl at each time interval shown below.

Time / seconds	*0*	*10*	*20*	*30*	*40*	*50*	*60*
Mass of vessel / g	*411.02*	*410.42*	*409.84*	*409.25*	*408.65*	*408.08*	*407.51*

Tip: You'll need the ideal gas equation for this question. It's: $pV = nRT$.

Q4 A student is following the reaction between 100 cm³ 1.00 mol dm⁻³ sulfuric acid and 15.0 g of solid sodium carbonate, by monitoring the volume of gas produced at r.t.p.. She takes measurements at 15 second intervals. Her results are recorded in the table below.
Calculate the concentration of H_2SO_4 at each time point.

Time / seconds	*0*	*15*	*30*	*45*	*60*	*75*
Volume of gas produced / cm³	*0.00*	*3.20*	*6.51*	*9.94*	*13.0*	*15.9*

Practice Questions — Fact Recall

Q1 What is meant by the term 'continuous monitoring'?

Q2 Draw and label the set-up you would use to measure the volume of gas produced over the course of a reaction.

Q3 What does a colorimeter measure?

Q4 Describe how you could follow the rate of reaction for a reaction where a gas is lost from the reaction container.

2. Concentration-Time Graphs

Once you've converted the data you've collected from continuously monitoring a reaction into concentration data, you can plot a concentration-time graph. You can use the gradient of the line of this graph to work out the reaction rate.

Gradients of straight-line graphs

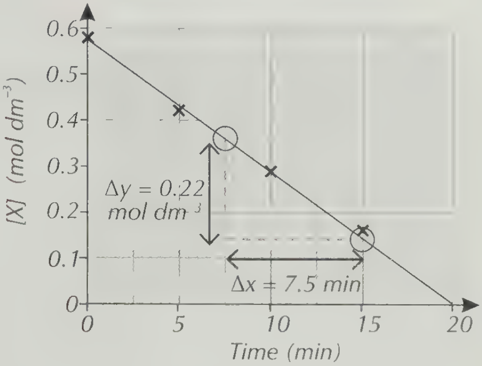
You can use the data from a continuous monitoring experiment to plot a graph of concentration against time. The rate at any point is given by the gradient at that point on this concentration-time graph.

You work out the gradient using this equation:

$$\text{gradient} = \text{change in } y \div \text{change in } x$$

Example — **Maths Skills**

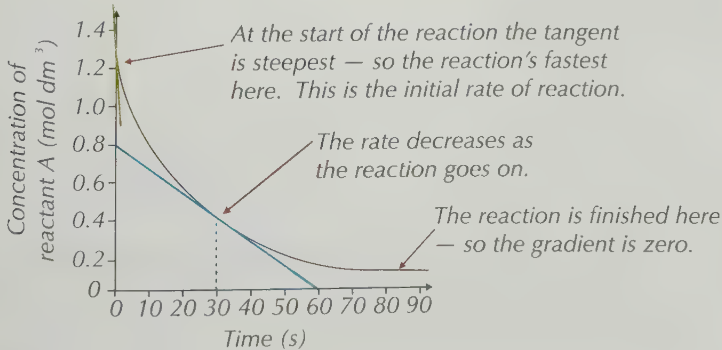
A concentration-time graph for a reactant, X, is shown below. Work out the rate of the reaction.



1. The concentration-time graph is a straight-line graph, so the gradient is the same at all points on the line.
2. Pick two points on the line of best fit that pass through the corners of the squares, and so are easy to read.
3. Use the equation, gradient = change in $y \div$ change in x, to work out the gradient of the graph.
   gradient = $0.22 \div 7.5 = 0.029$ mol dm^{-3} min^{-1}
4. So the rate of reaction is 0.029 mol dm^{-3} min^{-1}.

Gradients of curved graphs

If the rate of a reaction changes over time, then the concentration-time graph will be a curve, like the one in Figure 1.



At the start of the reaction the tangent is steepest — so the reaction's fastest here. This is the initial rate of reaction.

The rate decreases as the reaction goes on.

The reaction is finished here — so the gradient is zero.

Figure 1: *Graph showing the concentration of a reactant against time.*

Learning Objectives:

- Be able to calculate the rate of a reaction from the measurement of the gradient of a concentration-time graph.

Specification Reference 5.1.1

Tip: Don't forget, the x-axis is the horizontal axis and the y-axis is the vertical axis.

Tip: 'Δ' means 'the change in', so Δx is the change in x, and Δy is the change in y.

Tip: Square brackets, [ ], mean something is a concentration, so [X] is the concentration of reactant X.

Tip: Look back at pages 18-19 for more on calculating gradients from concentration-time graphs.

Tip: For the reaction in Figure 1, the rate of reaction slows down as time progresses. This is because the reactants get used up, and so collisions between reactant molecules become less likely.

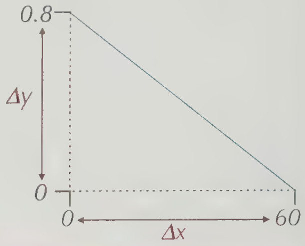
If the graph's a curve, to find the rate you have to draw a tangent to the curve at the point you're interested in and find the gradient of that. A tangent is a line that just touches a curve and has the same gradient as the curve does at that point. The gradient of a tangent is the change in vertical height divided by the change in horizontal width.

Tip: The sign of the gradient doesn't really matter — it's a negative gradient when you're measuring the reactant concentration because the reactant decreases. If you measured the product concentration, it'd be a positive gradient.

Example — Maths Skills

The gradient of the blue tangent on the graph in Figure 1 is the rate of reaction at 30 seconds. This tangent makes a triangle with the *y*-axis and the *x*-axis. The change in *y* is –0.8 and the change in *x* is 60, so:

$$\text{Gradient} = \frac{\Delta y}{\Delta x} = \frac{-0.8}{60} = -0.013 \text{ mol dm}^{-3}\text{ s}^{-1}$$

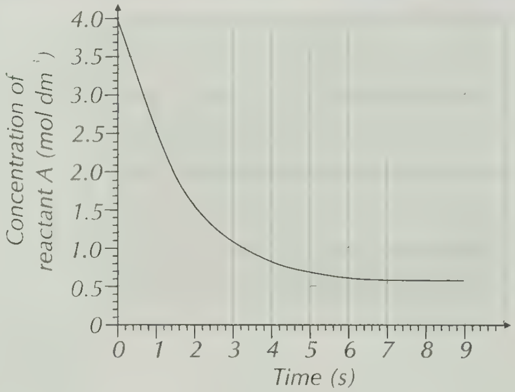


This means that the rate of reaction at 30 seconds is **0.013 mol dm^{-3} s^{-1}**.

Practice Questions — Application

Tip: To draw a tangent to a curve, place a ruler at the point where you're measuring the gradient so that it's just touching the curve. Position the ruler so that you can see the whole curve. Adjust the ruler until the space between the ruler and the curve is equal on both sides of the point. Then draw your tangent.

Q1 The concentration-time graph for a reaction is shown below:



Determine the rate of this reaction after:

a) 1 second b) 2 seconds c) 4 seconds

Q2 A student is measuring the volume of carbon dioxide gas formed by a reaction between limestone and hydrochloric acid. Her results are shown in the following table.

Tip: There's a lot to remember when it comes to drawing graphs. You've got to think about the size of the graph, what goes on which axis, the scale, not to mention making sure you plot the data points correctly.

Time / minutes	0	1	2	3	4	5
Concentration of acid / mol dm^{-3}	5.0	3.1	2.6	2.5	2.4	2.4

a) Plot the data in the table on a graph.

b) Draw a line of best fit on the graph drawn in part a).

c) Calculate the rate of the reaction at 2 minutes.

Practice Question — Fact Recall

Q1 Explain how you could determine the rate of reaction at a particular time using a concentration-time graph.

3. Initial Rates

You can find the initial rate of a reaction from a concentration-time graph. This is a faff if you want to find how the initial rate changes with initial concentrations of the reactants, so the initial rates method is often used instead.

Learning Objective:

- Understand the techniques and procedures used to investigate reaction rates using the initial rates method (PAG 10).

Specification Reference 5.1.1

Finding the initial rate

The initial rate of a reaction is the rate right at the start of the reaction. You can find this from a concentration-time graph by calculating the gradient of the tangent at time = 0 (see Figure 1).

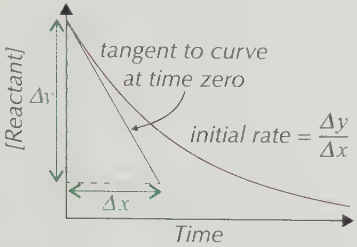
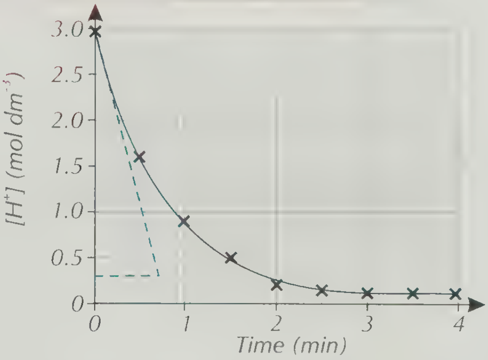


Figure 1: *Graph showing how to calculate the initial rate of reaction.*

Example — Maths Skills

The graph on the right shows the change in concentration of H^+ ions over time in a reaction between a metal and an acid. To work out the initial rate, you need to work out the gradient of the curve right at the start of the reaction.



- Draw a tangent to the curve at time = 0.
- Work out the gradient of the tangent using the method on p. 293-294.

  gradient = change in y ÷ change in x = (0.3 – 3.0) ÷ (0.7 – 0.0)

  = –2.7 mol dm^{-3} ÷ 0.7 mins = –3.875... mol dm^{-3} min^{1}
- So the initial rate of reaction was **3.9 mol dm^{-3} min^{-1}**.

Tip: The gradient of the tangent is negative as it slopes down from left to right. You can ignore this when writing down what the rate of the reaction is though — you don't get negative rates of reaction.

The initial rates method

PRACTICAL ACTIVITY GROUP 10

Another way of finding the initial rate of a reaction is the **initial rates method**. This method is often used to find how the initial rate varies as you change the initial concentration of one of the reactants, as it's easier than doing multiple continuous monitoring experiments and finding each initial rate from a concentration-time graph. In the initial rates method, you time how long it takes for a set amount of product to form at the beginning of the reaction in order to calculate an initial rate for a reaction. For example, for reactions that produce a precipitate, you can measure the time it takes for a mark underneath the reaction vessel to disappear from view at varying concentrations of the reactants. Or, for a reaction that produces a gas, you could time how long it takes for a set amount of the gas to form. When you plan an experiment like this, you need to ensure that the rate won't change much over the time period of your experiment — otherwise you can't assume that your results give you an indication of the initial rate of your experiment.

Tip: If you're using the initial rates method, you don't have to keep measuring until the reaction is completely over — you just need enough data to be able to work out the rate at the beginning of the reaction.

Once you've collected your data, you can work out the initial rate of the reaction by doing the following calculations:

- Work out how many moles of product there are in the set amount that you measure in each reaction. This will be the same for each of your experiments, as the same amount of product always forms.
- Use the reaction equation to work out how many moles of the reactant you're interested in will have been used up when the set amount of product has formed. Again, this will be the same for each of the experiments.
- Divide this by the volume of the reaction mixture to calculate the change in concentration of your reactant.
- Divide the change in concentration of the reactant by the time taken for the set amount of product to form. This is the initial rate of your reaction.

By changing the initial concentrations of each reactant, and working out each initial rate, you'll get data similar to that shown in the example below. This can be used to work out reaction orders and rate constants.

Example

A student is investigating how the initial rate of the following reaction changes as he varies the concentration of hydrochloric acid:

$$Mg_{(s)} + 2HCl_{(aq)} \rightarrow MgCl_{2(aq)} + H_{2(g)}$$

For each concentration of HCl, he starts with 15 cm^3 acid and a 5 cm length of magnesium ribbon. He times how long it takes for 10 cm^3 of $H_{2(g)}$ to be produced at each concentration of HCl. His results are shown in the table.

Initial concentration HCl / mol dm^{-3}	Time to produce 10 cm^3 $H_{2(g)}$ / s
3.00	79
2.00	131
1.50	144
0.800	222

- The number of moles of H_2 formed in each reaction can be calculated by rearranging the ideal gas equation:

$$pV = nRT \longrightarrow n = (pV) \div (RT)$$

$n = [(1.0 \times 10^5) \times (10 \div 1\,000\,000)] \div (8.31 \times 298) = 0.000403...$ mol

- From the reaction equation, you can see that for every mole of $H_{2(g)}$ that forms, 2 moles of $HCl_{(aq)}$ will have reacted.
  So the number of moles of $HCl_{(aq)}$ that react to form 10 cm^3 of $H_{2(g)}$ is 0.000403... × 2 = 0.000807... moles.
- The reaction mixture is always 15 cm^3, so the change in concentration for each experiment is 0.000807... ÷ (15 ÷ 1000) = 0.0538... mol dm^{-3}.
- The initial rate of each reaction can now be calculated by dividing 0.0538... mol dm^{-3} by the time taken for the reaction to finish.

Initial concentration HCl / mol dm^{-3}	Time to produce 10 cm^3 $H_{2(g)}$ / s	Initial rate / mol dm^{-3} s^{-1}
3.00	79	0.000682
2.00	131	0.000411
1.50	144	0.000374
0.800	222	0.000243

Tip: If you're going to do an initial rates experiment, don't forget to carry out a risk assessment first.

Figure 2: Students measuring the rate of a reaction that has a gaseous product.

Tip: In the ideal gas equation, pressure is in Pa, volume is in m^3, temperature is in K and the gas constant is 8.31 J mol^{-1} K^{-1}.

Tip: The rate of production of H_2 for each experiment is just 10 cm^3 (the volume produced) divided by the time taken to produce this volume in units of cm^3 s^{-1}.

Tip: 1/time is proportional to the reaction rate. You can therefore use (1 ÷ time) to give you a measure of the rate in units of, e.g. s^{-1}.

Tip: You can use this data to draw a rate-concentration graph which can tell you lots about the reaction (see pages 301 and 306).

Clock reactions

PRACTICAL ACTIVITY GROUP 10

A particular type of initial rates reactions are **clock reactions**. Here, the formation of a set amount of product is shown by a sudden, visual change in the reaction mixture. This works by adding a known amount of a substance that reacts with the product you're interested in to the reaction vessel. To begin with, this substance reacts immediately with the product as it forms. As soon as the substance is used up, the presence of unreacted product in the reaction vessel causes a sudden change, such as a colour change. This is the endpoint of the reaction. The quicker the endpoint is reached, the faster the initial rate of the reaction.

Tip: When carrying out clock reactions, the data you collect will be in units of time, rather than units of rate. You can use 1/time as a measure of the rate.

When carrying out a clock reaction, you need to make the following assumptions:

- The concentration of each reactant doesn't change significantly over the time period of your clock reaction.
- The temperature stays constant.
- When the endpoint is seen, the reaction has not proceeded too far.

As long as these assumptions are reasonable for your experiment, you can assume that the rate of reaction stays constant during the time period of your measurement. So the rate of your clock reaction will be a good estimate for the initial rate of your reaction.

Example

The most famous clock reaction is the iodine clock reaction. The reaction you're monitoring is:

$$H_2O_{2\,(aq)} + 2I_{(aq)} + 2H^{+}_{(aq)} \rightarrow 2H_2O_{(l)} + I_{2\,(aq)}$$

- Small amounts of sodium thiosulfate solution and starch are added to an excess of hydrogen peroxide and iodide ions in acid solution. Starch is used as an indicator — it turns blue-black in the presence of iodine.
- The sodium thiosulfate that is added to the reaction mixture reacts instantaneously with any iodine that forms:

$$2S_2O_3{}^{2-}{}_{(aq)} + I_{2\,(aq)} \rightarrow 2I^{-}_{(aq)} + S_4O_6{}^{2-}{}_{(aq)}$$

- To begin with, all the iodine that forms in the first reaction is used up straight away in the second reaction. But once all the sodium thiosulfate is used up, any more iodine that forms will stay in solution, so the starch indicator will suddenly turn the solution blue-black. This is the end of the clock reaction.
- Varying iodide or hydrogen peroxide concentration while keeping the others constant will give different times for the colour change.

Tip: These are ionic equations — they only show the reacting particles. You met them on pages 66-67.

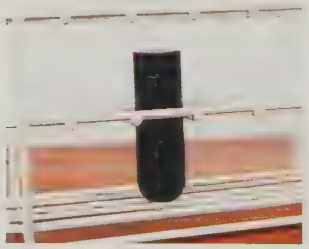
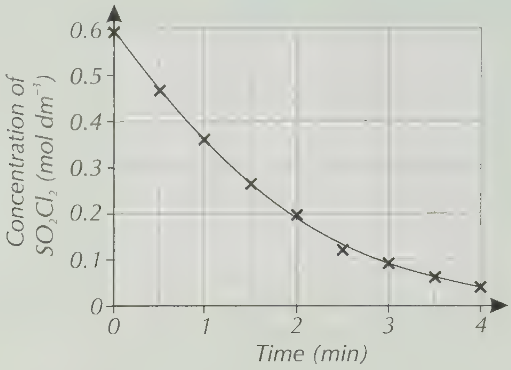


Figure 3: *A solution containing starch turns blue-black when iodine is present.*

Tip: Colorimetry is a great way of monitoring the iodine clock reaction due to the change in colour of the starch indicator when iodine is present. Since this change is very sudden, you could also monitor the reaction by eye.

Practice Questions — Application

Q1 The data on the graph below was obtained experimentally from the decomposition of SO_2Cl_2. Work out the initial rate of the reaction.



Q2 A student is carrying out an initial rates reaction to try and work out how the rate of the following reaction depends on the initial concentrations of the reactants:

$$Mg_{(s)} + 2HCl_{(aq)} \rightarrow MgCl_{2\,(aq)} + H_{2\,(g)}$$

He times how long it takes for 20 cm³ of hydrogen gas to be formed at varying concentrations of HCl. His results are in the table below.

Trial number	[HCl] / mol dm^{-3}	Time to produce 20 cm³ $H_{2(g)}$ / s
1	1.25	5.1
2	0.800	15.3
3	0.500	31.5

Work out the initial rate of each reaction in cm³ s^{-1}.

Tip: If you need some help calculating the gradients of graphs, have a look back at pages 293-294, or page 553 in the Maths Skills section.

Practice Questions — Fact Recall

Q1 How do you find out the initial rate of a reaction from a concentration-time graph?

Q2 Give three assumptions you need to make when calculating the initial rate of reaction using a clock reaction.

4. Reaction Orders

Reaction orders tell you how the rate of a reaction will be affected if you change the concentration of a reactant. Each reactant has its own order, and you can work them out with the help of a few experiments.

What are reaction orders?

The **reaction order**, or **order of reaction** with respect to a particular reactant tells you how the reactant's concentration affects the rate.

- If you double the reactant's concentration and the rate stays the same, the order with respect to that reactant is 0 (the reaction is zero order with respect to the reactant).
- If you double the reactant's concentration and the rate also doubles, the order with respect to that reactant is 1 (the reaction is first order with respect to the reactant).
- If you double the reactant's concentration and the rate quadruples, the order with respect to that reactant is 2 (the reaction is second order with respect to the reactant).

A reaction will also have an **overall order**. This is the sum of the orders of all the different reactants. So if there are two reactants in an reaction, and one has an order of 1 and another has an order of 2, then the overall order of the reaction will be 3.

Finding the orders of reactants in a reaction

You can only find orders of reaction from experiments.
You can't work them out from chemical equations.
Think about the generic reaction:

$$A + B \rightarrow C$$

To find the order of each reactant in a reaction, you have to monitor how each reactant affects the rate one by one. So first, you would want to find out the order of the reaction with respect to the concentration of A. You have to use experimental data to work out the order, and you've got two options. You could continuously monitor the change in concentration of A against time to construct a concentration-time graph and then a rate-concentration graph (see pages 300-301), or you could use the initial rates method (see pages 295-296) to find out how the initial rate changes as you vary the concentration of A.

If you decide to monitor your reactions using continuous monitoring, you have to make sure that the concentrations of any reactants you're not investigating, here it's just B, are in excess — there's loads more B than there is A. This means the concentration of B won't change much during the reaction (it will be pretty much constant, and the reaction is effectively zero order with respect to B). Any change in the rate can therefore only be due to the change in concentration of A (the reactant you're investigating). To find the order of the reaction with respect to reactant B, you repeat the experiments, but this time varying the concentration of B and having reactant A in excess.

Learning Objectives:

- Be able to explain and use the terms order and overall order.
- Be able to deduce orders from experimental data.
- Be able to deduce the order (0 or 1) with respect to a reactant from the shape of the concentration-time graph of that reactant.
- Be able to deduce the order (0, 1 or 2) with respect to a reactant from the shape of the rate-concentration graph of that reactant.

Specification Reference 5.1.1

Tip: If reactant B is ten times more concentrated than reactant A, and they react in a 1:1 ratio, then in the time it takes for the concentration of reactant A to half, the concentration of reactant B will only have fallen by (50% ÷ 10) = 5%. This change will have a negligible effect on the rate compared to the change in concentration of reactant A.

Tip: If you're using the initial rates method, then remember to keep all the variables other than the concentration of the reactant constant, for example the temperature and the reaction volume.

Tip: There's information about different techniques you can use to follow reactions on pages 289-290.

Tip: Don't forget — if doubling the concentration doesn't affect the rate it's zero order, if doubling the concentration doubles the rate it's first order and if doubling the concentration quadruples the rate it's second order.

Exam Tip
You would usually only change one concentration at a time between experiments, but you could get a question where more than one concentration changes — don't get confused, the principle is the same.

Exam Tip
You need to be able to work out orders of reaction from initial rates data in the exam, so make sure you understand this example.

Tip: If you've measured something else other than concentration in your experiment (such as volume) you can either use your data along with the reaction equation to calculate the concentrations of the reactants left behind, or just plot a graph of the data you've measured against time (e.g. a volume-time graph). The shape should be the same as a concentration-time graph.

Reaction orders from experimental data

You met the initial rates method on pages 295-296 — it's used to see how the rate right at the start of a reaction changes if you change the starting concentration of one of the reactants. The initial rates method is a great way of working out the orders of different reactants in a reaction. To do this, you have to compare how the initial rate of the reaction changes as you change the initial concentration of one of the reactants using the steps on page 296. You then use this to work out the order for that reactant. You can then repeat the process for each reactant (different reactants may have different orders).

Example — Maths Skills

The table below shows the results of a series of initial rate experiments for the reaction $NO_{(g)} + CO_{(g)} + O_{2(g)} \rightarrow NO_{2(g)} + CO_{2(g)}$. Work out the reaction orders with respect to each reactant.

Experiment number	[NO] / mol dm^{-3}	[CO] / mol dm^{-3}	[O_2] / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
1	2.0×10^{-2}	1.0×10^{-2}	1.0×10^{-2}	0.16
2	1.0×10^{-2}	1.0×10^{-2}	1.0×10^{-2}	0.04
3	2.0×10^{-2}	2.0×10^{-2}	1.0×10^{-2}	0.16
4	4.0×10^{-2}	1.0×10^{-2}	2.0×10^{-2}	0.64

- Look at experiments 1 and 2 — when [NO] doubles (and all the other concentrations stay constant) the rate is four times faster. So the reaction is second order with respect to NO.
- Look at experiments 1 and 3 — when [CO] doubles (but all the other concentrations stay constant), the rate stays the same. So the reaction is zero order with respect to CO.
- Look at experiments 1 and 4 — the rate of experiment 4 is four times faster than experiment 1. The reaction is second order with respect to NO, so the rate will quadruple when you double [NO]. But in experiment 4, [O_2] has also been doubled. As doubling [O_2] hasn't had any additional effect on the rate, the reaction must be zero order with respect to O_2.

So, this reaction is second order with respect to NO, zero order with respect to CO and zero order with respect to O_2.

Finding reaction orders using graphs

You can work out the reaction order with respect to a particular reactant using a concentration-time graph, or a rate-concentration graph. Concentration-time graphs can be made by taking repeated measurements of the concentration of the reactant you are investigating during a reaction (continuous monitoring, page 289). You can make a rate-concentration graph using a concentration-time graph. Here's how:

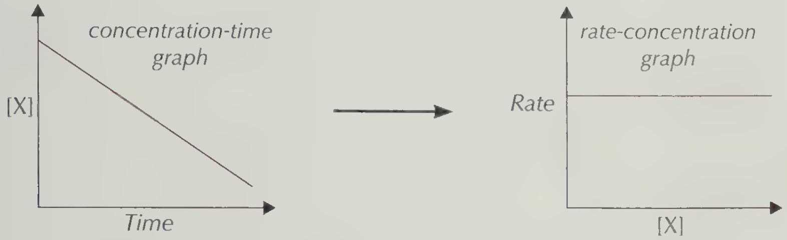
- Find the gradient (which is the rate) at various points along the concentration-time graph (see pages 293-294 for a reminder of how to do this). This gives you a set of points for the rate-concentration graph.
- Then just plot the points and join them up with a line or smooth curve.

You can also plot a rate-concentration graph using data obtained from initial rates experiments.

HOW SCIENCE WORKS

The shapes of rate-concentration graphs and concentration-time graphs tell you the order of the reaction with respect to the reactant you're investigating. This is because rate and concentration are correlated — changing the concentration of one of the reactants can have a direct effect on the rate of the reaction. This is a causal link, as reducing the concentration of a reactant will cause fewer collisions to occur, and so, unless the reactant is zero order, the rate of the reaction will decrease. How much the rate decreases as the concentration decreases (the order) is what determines the shape of rate-concentration or concentration-time graph.

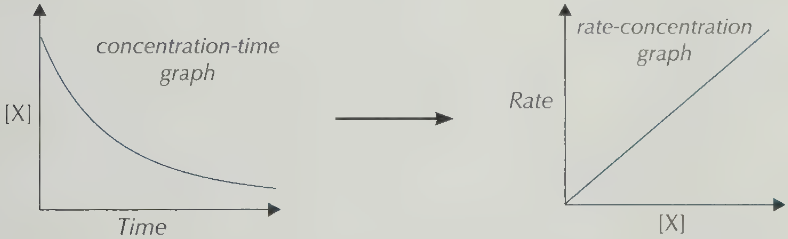
Zero order



Tip: If something is in [square brackets] it's a concentration. So [X] means the concentration of reactant X.

A horizontal line on a rate-concentration graph means that changing the concentration doesn't change the rate, so the reaction is zero order.

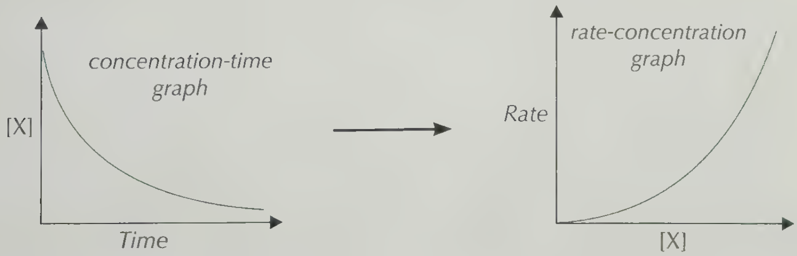
First order



If the rate-concentration graph is a straight line through the origin, then the reaction is first order. The rate is proportional to [X]. For example, if the concentration of X triples, the rate will triple. If it halves, the rate will halve.

Tip: You don't need to be able to recognise the shape of a concentration-time graph for a reaction that is second order with respect to one of its reactants. So if you're given a concentration-time graph of a reactant that is curved and asked to predict its order, it'll probably be first order.

Second order



A curved rate-concentration graph means that the reaction is second order. The rate is proportional to $[X]^2$. For example, if the concentration of X triples, the rate will be nine times as fast (because $3^2 = 9$).

Tip: In theory, a curved rate-concentration graph could mean a higher order than 2. But you won't be asked about any with a higher order than 2 in the exams — so if you see a curve, always say order 2.

Practice Questions — Application

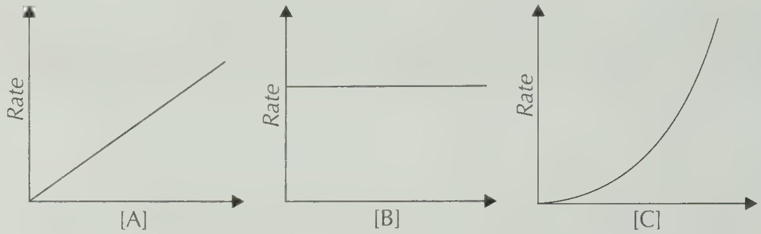
Q1 The results of a series of initial rate experiments for the following reaction are shown below: $O_3 + C_2H_4 \rightarrow 2CH_2O + \frac{1}{2}O_2$

Experiment number	$[O_3]$ / mol dm^{-3}	$[C_2H_4]$ / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
1	8.0×10^{-4}	8.0×10^{-4}	0.053
2	1.6×10^{-3}	8.0×10^{-4}	0.106
3	1.6×10^{-3}	2.4×10^{-3}	0.318

a) Determine the orders of reaction with respect to O_3 and C_2H_4.

b) What is the overall order of the reaction?

Q2 Below are the rate-concentration graphs produced as the concentrations of three different reactants (A, B and C) changed during a reaction.



a) Deduce the reaction orders with respect to reactants A, B and C.

b) State how you would expect the rate of reaction to change if the concentration of:

(i) A was halved (ii) B was tripled (iii) C was doubled

Q3 The results of a continuous monitoring experiment investigating the change in concentration of sodium hydroxide for the following reaction are shown below: $(CH_3)_3CBr + NaOH \rightarrow (CH_3)_3COH + NaBr$

Time / s	0	30	60	90	120
[NaOH] / mol dm^{-3}	0.500	0.465	0.429	0.382	0.349

Use the table to draw a concentration-time graph and determine the order of the reaction with respect to sodium hydroxide.

Q4 The table below shows the results of a series of initial rate experiments for the reaction: $2A + B + C \rightarrow AB + AC$

Experiment number	[A] / mol dm^{-3}	[B] / mol dm^{-3}	[C] / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
1	1.2	1.2	1.2	0.25
2	1.2	2.4	1.2	1.00
3	1.2	2.4	3.6	3.00
4	0.60	2.4	2.4	1.00

Determine the orders of reaction with respect to reactants A, B and C.

Practice Questions — Fact Recall

Q1 Explain what is meant by the term 'reaction order'.

Q2 a) Describe two methods you could use to produce a rate-concentration graph.

b) Explain how you could determine the order of reaction with respect to a reactant using a rate-concentration graph.

Exam Tip
Rate-concentration graphs and concentration-time graphs look similar, so if you're given one in the exam, make sure you double-check which it is before you start answering the question. You can tell the difference by looking at what's plotted on each of the axes.

Exam Tip
Make sure you get as much practice as you can with working out reaction orders using the initial rates method — you need to be confident with it if it comes up in the exams.

Tip: If you're given the time the reaction took, rather than the initial rate of the reaction, then 1/time is proportional to the rate, so you can compare these values to work out the order of the reaction with respect to a reactant.

5. Rate Equations

The rate of a reaction is linked to the concentrations of the reactants by something called a rate equation. This topic is all about rate equations and why they are useful. Have fun...

What are rate equations?

Rate equations look ghastly, but all they're really telling you is how the rate is affected by the concentrations of reactants. For a general reaction: A + B → C + D, the rate equation is:

$$\textbf{Rate} = k[\mathrm{A}]^m[\mathrm{B}]^n$$

The square brackets mean the concentration of whatever's inside them. So [A] means the concentration of A and [B] means the concentration of B. The units of rate are mol dm^{-3} s^{-1}. m and n are the **orders of reaction** (see page 299) and k is the **rate constant** — the bigger k is, the faster the reaction.

Writing rate equations

You need to know how to write rate equations for reactions. This example shows you how:

Example — Maths Skills

The chemical equation below shows the acid–catalysed reaction between propanone and iodine.

$$CH_3COCH_{3(aq)} + I_{2(aq)} \xrightarrow{H^+_{(aq)}} CH_3COCH_2I_{(aq)} + H^+_{(aq)} + I^-_{(aq)}$$

This reaction is first order with respect to propanone, first order with respect to $H^+_{(aq)}$ and zero order with respect to iodine. Write the rate equation for this reaction.

In this example there are three things that you need to think about — the orders of reaction of propanone (CH_3COCH_3), iodine (I_2) and hydrogen ions (H^+). (Even though H^+ is a catalyst, rather than a reactant, it can still be in the rate equation because it affects the rate of reaction.) So the rate equation will be in the form:

$$\text{Rate} = k[\mathrm{A}]^m[\mathrm{B}]^n[\mathrm{C}]^x$$

You're told the reaction orders with respect to each reactant in the question so just use that information to construct the rate equation:

$$\text{Rate} = k[CH_3COCH_3]^1[H^+]^1[I_2]^0$$

But $[X]^1$ is usually written as [X], and $[X]^0$ equals 1 so is usually left out of the rate equation. So you can simplify the rate equation to:

$$\text{Rate} = k[CH_3COCH_3][H^+]$$

This rate equation shows that the rate of reaction is proportional to the concentrations of propanone and H^+. So doubling the concentration of either propanone or H^+ will double the rate of the reaction.

Learning Objectives:

- Be able to explain and use the term rate constant.
- Be able to deduce a rate equation from orders of the form: rate = $k[\mathrm{A}]^m[\mathrm{B}]^n$, where m and n are 0, 1 or 2.

Specification Reference 5.1.1

Tip: There are only two reactants in this general equation, but you can write rate equations for equations with any number of reactants. E.g. if there are three reactants the equation is:

$$\text{Rate} = k[\mathrm{A}]^m[\mathrm{B}]^n[\mathrm{C}]^x$$

Exam Tip

m and n could take any value, but in the exam you'll only have to deal with rate equations where m and n are 0, 1 or 2.

Tip: The rate equation is a standard way of showing how rates relate to reactant concentrations and their orders. So, scientists all over the world understand its meaning.

Tip: When simplifying rate equations think about the indices laws from maths (see page 551) — the same rules apply here. Anything to the power of zero is one (e.g. $[X]^0 = 1$) and anything to the power of one doesn't change (e.g. $[X]^1 = [X]$).

Tip: Remember, you can only find the order of reactions, and so rate equations, by doing experiments. You can't work them out from a balanced chemical equation.

Exam Tip
In the exams, you might be asked to predict a rate of reaction after having written the rate equation and calculated a value for k — so make sure you know how to do it.

Tip: Before you calculate the rate of a reaction, you may first have to determine the value of the rate constant. See pages 305-307 for how to do this.

Figure 1: The reaction between $Na_2S_2O_3$ and HCl. The solution turns cloudy as the reaction progresses which allows the rate of reaction to be measured.

Predicting the rate of a reaction

If you know the rate constant and the rate equation for a particular reaction at a certain temperature, you can use them to predict the rate of reaction for given reactant concentrations at this temperature. All you have to do is substitute values into the rate equation and solve to find the rate.

Example — Maths Skills

The reaction $2HI \rightarrow H_2 + I_2$ is second order with respect to hydrogen iodide. Construct a rate equation for this reaction and calculate the rate when the concentration of HI is 0.0200 mol dm^{-3} given that at the reaction temperature, the rate constant, $k = 1.11 \times 10^{-19}$ mol dm^{-3} s^{-1}.

The reaction is second order with respect to HI, so the rate equation is:

$$\text{Rate} = k[\text{HI}]^2$$

To calculate the rate of the reaction when [HI] = 0.0200 mol dm^{-3}, you just have to substitute the value of the concentration of HI and the value of the rate constant into the expression for the rate equation:

$$\text{Rate} = 1.11 \times 10^{-19} \times (0.0200)^2 = \mathbf{4.44 \times 10^{-23}\ mol\ dm^{-3}\ s^{-1}}$$

Practice Question — Application

Q1 The following reaction occurs between sodium thiosulfate ($Na_2S_2O_3$) and hydrochloric acid:

$$Na_2S_2O_{3(aq)} + 2HCl_{(aq)} \rightarrow 2NaCl_{(aq)} + S_{(s)} + SO_{2(g)} + H_2O_{(l)}$$

This reaction is first order with respect to $Na_2S_2O_3$ and zero order with respect to HCl.

a) Construct the rate equation for this reaction.

b) Given that the rate constant, $k = 4.67 \times 10^{-1}$ s^{-1} at 298 K, calculate the rate of the reaction when the concentration of sodium thiosulfate is 0.45 mol dm^{-3} and the concentration of hydrochloric acid is 0.60 mol dm^{-3}.

Practice Questions — Fact Recall

Q1 What does the rate equation tell you?

Q2 In the rate equation, Rate = $k[A]^m[B]^n$, what do the following represent:

a) k? b) [A]? c) m?

Q3 Write the general rate equation for a reaction which has 3 reactants.

6. The Rate Constant

The rate constant, k, is the value in the rate equation that links the concentration and the order of each of the reactants to the rate of the reaction. To start, you need to know how to find it using experimental data.

Using the rate equation to find *k*

If you know the orders of a reaction, you can use the rate equation and experimental data to work out the rate constant, *k*. The units of *k* vary, so you'll need to work them out too.

Example — Maths Skills

The reaction below is second order with respect to NO and zero order with respect to CO and O_2.

$$NO_{(g)} + CO_{(g)} + O_{2(g)} \rightarrow NO_{2(g)} + CO_{2(g)}$$

At a certain temperature, the rate is 1.76×10^{-3} mol dm^{-3} s^{-1}, when $[NO_{(g)}] = [CO_{(g)}] = [O_{2(g)}] = 2.00 \times 10^{-3}$ mol dm^{-3}.
Find the value of the rate constant, *k*, at this temperature.

- To answer this question you first need to write out the rate equation:

$$\text{Rate} = k[NO]^2[CO]^0[O_2]^0$$
$$= k[NO]^2$$

- Next insert the concentration and the rate, which were given to you in the question:

$$\text{Rate} = k[NO]^2$$
$$1.76 \times 10^{-3} = k \times (2.00 \times 10^{-3})^2$$

- Rearrange the equation and calculate the value of *k*:

$$k = \frac{1.76 \times 10^{-3}}{(2.00 \times 10^{-3})^2} = 440$$

- Find the units of *k* by putting the other units in the rate equation:

$$\text{Rate} = k[NO]^2 \quad \text{so} \quad \text{mol dm}^{-3}\text{ s}^{-1} = k \times (\text{mol dm}^{-3})^2$$

- Rearrange the equation to get *k*:

$$k = \frac{\text{mol dm}^{-3}\text{ s}^{-1}}{(\text{mol dm}^{-3})^2}$$

- Cancel out units wherever possible. In this example you can cancel out a mol dm^{-3} from the top and bottom lines of the fraction:

$$k = \frac{\cancel{\text{mol dm}^{-3}}\text{ s}^{-1}}{(\cancel{\text{mol dm}^{-3}})(\text{mol dm}^{-3})} = \frac{\text{s}^{-1}}{\text{mol dm}^{-3}}$$

- Get rid of the fraction using index laws:

$$k = \frac{\text{s}^{-1}}{\text{mol dm}^{-3}} = \text{mol}^{-1}\text{ dm}^{3}\text{ s}^{-1}$$

- So the answer is:

$$k = 440 \text{ mol}^{-1}\text{ dm}^{3}\text{ s}^{-1}$$

Learning Objectives:

- Be able to calculate the rate constant, *k*, and related quantities from a rate equation, including determination of units.
- Be able to determine the rate constant for a first order reaction from the gradient of a rate-concentration graph.
- Be able to explain and use the term half-life.
- Be able to measure the constant half-life, $t_{1/2}$, from the concentration-time graph of a first order reaction.
- Be able to determine the rate constant, *k*, for a first order reaction from the constant half-life, $t_{1/2}$, using the relationship: $k = \ln 2/t_{1/2}$.

Specification Reference 5.1.1

Tip: You need to know how to work out what units your answer is in — it crops up a lot in this section so it's important that you understand how to do it. Have a look at page 550 for more on finding units.

Tip: Index laws state that to move a number from the bottom of a fraction to the top of a fraction, you just have to change the signs of the powers. So if you've got a mol^2 dm^{-6} on the bottom of the fraction it becomes mol^{-2} dm^6 when it's on the top.

Tip: The value of k depends on the temperature (see pages 313-314), so predicted rates of reaction will only be accurate if the reaction is performed at the same temperature as the reaction used to calculate k.

Once you've found the rate constant for a reaction, you can use it in the rate equation to predict the rate of the reaction at the same temperature but with different concentrations of reactants.

Example **Maths Skills**

On the previous page, you saw that the rate equation for the reaction $NO_{(g)} + CO_{(g)} + O_{2(g)} \rightarrow NO_{2(g)} + CO_{2(g)}$ is rate = $k[NO]^2$ and you worked out that the rate constant for the reaction is 440 $mol^{-1}\ dm^3\ s^{-1}$.

Calculate the rate of reaction if the concentration of NO is 0.00500 mol dm^{-3}.

$$\text{Rate} = k[NO]^2$$
$$= 440 \times (0.00500)^2$$
$$= \mathbf{0.0110\ mol\ dm^{-3}\ s^{-1}}$$

Rate constants of first order reactions

If you're asked to calculate the rate constant of a first order reaction, there are a few special methods you can use that won't work for reactions with different orders.

Calculating the rate constant from a rate-concentration graph

Tip: Rate-concentration graphs of a first order reactions are straight-line graphs (see page 301).

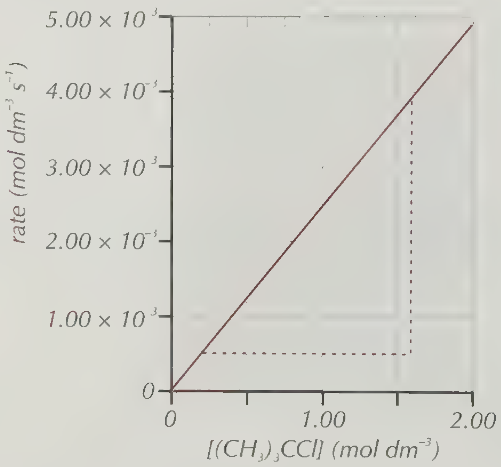
If the overall reaction is first order, then the rate constant is equal to the gradient of the rate-concentration graph of that reactant.

Example **Maths Skills**

The graph below shows how the rate of the following reaction depends on the concentration of 2-chloro-2-methylpropane $[(CH_3)_3CCl]$ in the following reaction:

$$(CH_3)_3CCl + NaOH \rightarrow (CH_3)_3COH + NaCl$$

Use the graph to calculate the rate constant, k, of this reaction.



Tip: The rate equation of a first order reaction is: rate = k[X], so a graph of rate against [X] has a gradient equal to the rate constant, k.

The rate-concentration graph is a straight line, so the reaction is first order and the rate constant is equal to the gradient of the graph.

$$\text{Gradient} = \frac{\text{change in } y}{\text{change in } x} = \frac{(3.90 \times 10^{-3}) - (0.50 \times 10^{-3})}{1.60 - 0.20} = \frac{3.40 \times 10^{-3}}{1.40}$$
$$= 2.43 \times 10^{-3}$$

The units of y are mol $dm^3\ s^{-1}$, and the units of x are mol dm^{-3}.

So the units of k are $\frac{mol\ dm^3\ s^{-1}}{mol\ dm^3} = s^{-1}$.

So k = $\mathbf{2.43 \times 10^{-3}\ s^{-1}}$

Calculating the rate constant from the half-life

The **half-life** of a reaction is the time it takes for half of the reactant to be used up. You can work out the half-life from a concentration-time graph (see Figure 1). All you have to do is read off the graph how long it takes for the concentration of the reactant to halve.

Tip: Half-life can also be written as $t_{1/2}$.

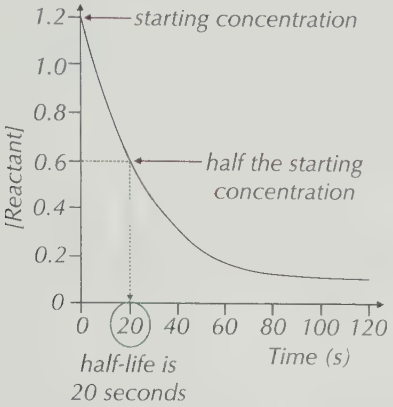


Figure 1: Graph showing how to work out the half-life of a reaction.

Tip: Lots of natural processes are first order reactions and so have a constant half-life. E.g. when a radioactive substance decays or a drug is broken down in the body the half-life is usually constant.

The half-life of a first order reaction is independent of the concentration. This means that the half life is constant (the same) no matter what the concentration is. This is only true for first order reactions — so if you see a reaction with a constant half-life, you know it must be first order. If you know the half-life of a first order reaction you can work out the rate constant using the equation:

$$\boxed{k = \frac{\ln 2}{t_{1/2}}}$$

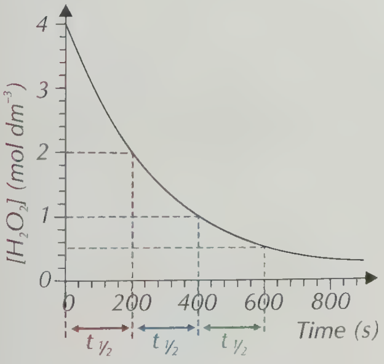
The units of k are: $\frac{\text{no units}}{\text{s}} = \text{s}^{-1}$

Figure 2: A Geiger counter measuring radioactive decay, which is a first order reaction.

Tip: 'ln x' means the natural logarithm of x. It's the opposite of 'e^x'. You'll need a scientific calculator to work it out. See pages 551-552 in the Maths Skills section for more on logs and powers.

Example — **Maths Skills**

This graph shows the decomposition of hydrogen peroxide, H_2O_2. Use the graph to measure the half-life at various points and work out the rate constant of the reaction.



$[H_2O_2]$ from 4 to 2 mol dm^{-3} = 200 s,
$[H_2O_2]$ from 2 to 1 mol dm^{-3} = 200 s,
$[H_2O_2]$ from 1 to 0.5 mol dm^{-3} = 200 s.

The half-life is always 200 s, regardless of the concentration, so it's a first order reaction with respect to $[H_2O_2]$.

The rate constant is: $k = \frac{\ln 2}{t_{1/2}} = \frac{\ln 2}{200\text{ s}} = \mathbf{3.47 \times 10^{-3}\ s^{-1}}$

Tip: You can measure the half-life between any two concentrations as long as the concentration halves — for example, you could also measure the half-life from 3 to 1.5 mol dm^{-3} and it should be the same.

Exam Tip
When answering calculation questions like these always remember to give the units for your answer.

Practice Questions — Application

Q1 The reaction below is second order with respect to NO and first order with respect to Cl_2:

$$2NO_{(g)} + Cl_{2(g)} \rightarrow 2NOCl_{(g)}$$

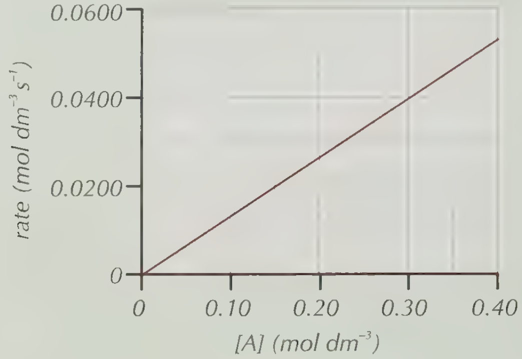
The rate of reaction is 5.85×10^{-6} mol dm^{-3} s^{-1} at 50 °C, when the concentration of both NO and Cl_2 is 0.400 mol dm^{-3}.

a) Write the rate equation for this reaction.

b) Calculate the rate constant (k) for this reaction at 50 °C.

c) Calculate the expected rate of reaction if 0.500 mol dm^{-3} NO were mixed with 0.200 mol dm^{-3} Cl_2 at 50 °C.

Q2 The following graph shows a plot of rate against concentration for a first order reaction. Calculate the rate constant of the reaction.



Tip: Remember to convert all your values into standard units (seconds for time, mol dm^{-3} for concentration) before you start any calculations.

Q3 The table below shows the results of an experiment to investigate the decomposition of ozone: $O_3 \rightarrow O_2 + O$

Time / min	0.0	3.0	6.0	9.0	12.0	15.0	18.0
Concentration / mol dm^{-3}	0.24	0.14	0.085	0.050	0.035	0.020	0.015

a) Plot a graph of these results, and determine the first three half-lives of the reaction.

b) What is the rate constant of this reaction?

Practice Questions — Fact Recall

Q1 How could you find the rate constant of a first order reaction from a rate-concentration graph?

Q2 Define the half-life of a reaction.

Q3 Give the equation that links the half-life of a first order reaction to its rate constant.

7. The Rate-Determining Step

Reaction mechanisms show step by step how a chemical reaction takes place. The most important step is the rate-determining step — that's what these pages are all about.

What is the rate-determining step?

Reaction mechanisms can have one step or a series of steps. In a series of steps, each step can have a different rate. The overall rate is decided by the step with the slowest rate — the **rate-determining step**.

The rate equation is handy for working out the mechanism of a chemical reaction. You need to be able to pick out which reactants from the chemical equation are involved in the rate-determining step. Here's how:

- If a reactant appears in the rate equation, it must affect the rate. So this reactant, or something derived from it, must be in the rate-determining step.
- If a reactant doesn't appear in the rate equation, then it won't be involved in the rate-determining step and neither will anything derived from it.

An important point to remember about rate-determining steps and mechanisms is that the rate-determining step doesn't have to be the first step in a mechanism. Also, the reaction mechanism can't usually be predicted from just the chemical equation — you need information about the orders of the reactants as well, which you can only get from doing experiments.

Predicting rate equations

The order of a reaction with respect to a reactant shows the number of molecules of that reactant that are involved in the rate-determining step. So, if a reaction's second order with respect to X, there'll be two molecules of X in the rate-determining step. This link means that if you know the rate determining step of a reaction, you can predict the rate equation.

Example

The mechanism for the reaction between chlorine radicals (Cl•) and ozone (O_3) consists of two steps:

$Cl\bullet_{(g)} + O_{3(g)} \rightarrow ClO\bullet + O_{2(g)}$ *This step is slow — it's the rate determining step.*

$ClO\bullet_{(g)} + O\bullet_{(g)} \rightarrow Cl\bullet + O_{2(g)}$ *This step is fast.*

Cl• and O_3 are both in the rate-determining step so must both be in the rate equation. So, the rate equation will be:

$$\text{Rate} = k[Cl\bullet]^m[O_3]^n$$

There's only one Cl• and one O_3 molecule in the rate-determining step, so the orders, *m* and *n*, are both 1. So the rate equation is:

$$\text{Rate} = k[Cl\bullet][O_3]$$

Predicting reaction mechanisms

If you know the rate equation you can predict which reactants are in the rate-determining step, and if you know which reactants are in the rate-determining step, you can work out the reaction mechanism. There's an example coming up on the next page to show you how.

Learning Objectives:

- Be able to explain and use the term rate-determining step.
- Be able to predict a rate equation for a multi-step reaction that is consistent with the rate-determining step.
- Be able to predict possible steps in a reaction mechanism of a multi-step reaction from the rate equation and the balanced equation for the overall reaction.

Specification Reference 5.1.1

Tip: You might also see the rate-determining step being called the rate-limiting step.

Tip: Catalysts can appear in rate equations, so they can be part of the rate-determining step too.

Tip: Have a look back at page 259 for more detail on how chlorine radicals catalyse the break-down of ozone in the stratosphere.

Exam Tip
In the exams, you might be asked to write the rate equation for a reaction from the rate-determining step so make sure you know what you're doing.

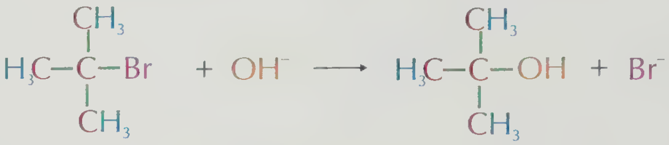
Tip: Experimental evidence about reaction orders is often used to develop theories for what the mechanism of a reaction will be.

Tip: You need to be sure that you understand rate equations before tackling this, or it won't make sense. If you need a reminder, flip back to page 303 and have a quick glance over the relevant bits.

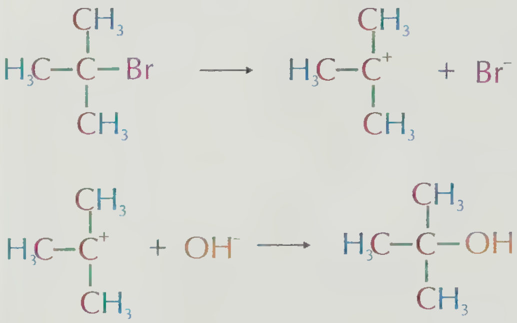
Example

2-bromo-2-methylpropane can react with the nucleophile OH^- to give 2-methylpropan-2-ol and bromide ions (Br^-).

There are two possible mechanisms for this reaction. Here's one...



... and here's the other one:



The actual rate equation was worked out using rate experiments. It is:

$$\text{Rate} = k[(CH_3)_3CBr]$$

OH^- isn't in the rate equation, so it can't be involved in the rate-determining step. The second mechanism is likely to be correct because there is one molecule of $(CH_3)CBr$ and no molecules of OH^- in the rate-determining step — just like the rate equation suggests.

Tip: This reaction is zero order with respect to OH^-. Changing the concentration of OH^- ions won't change the reaction rate.

If you're suggesting a mechanism, watch out — the most obvious answer might not always be the right one.

Example

When nitrogen(V) oxide, N_2O_5, decomposes, it forms nitrogen(IV) oxide and oxygen:

$$2N_2O_{5(g)} \rightarrow 4NO_{2(g)} + O_{2(g)}$$

From the chemical equation, it looks like two N_2O_5 molecules react with each other. So that might be your first idea — a simple one-step mechanism. The rate equation for this mechanism would be: rate = $k[N_2O_5]^2$.

But, experimentally, it's been found that the reaction is first order with respect to N_2O_5 — the rate equation is: rate = $k[N_2O_5]$.

This shows that there's only one molecule of N_2O_5 in the rate-determining step. So a one-step mechanism can't be right (a one-step mechanism would have two molecules of N_2O_5 in the rate-determining step).

One possible mechanism that fits the rate equation is:

$$N_2O_{5(g)} \rightarrow NO_{2(g)} + NO_{3(g)} \qquad \textit{slow (rate-determining step)}$$

$$NO_{3(g)} + N_2O_{5(g)} \rightarrow 3NO_{2(g)} + O_{2(g)} \qquad \textit{fast}$$

In this mechanism, only one molecule of N_2O_5 is in the rate-determining step — this fits in with the rate equation.

Tip: When you've come up with a mechanism, don't forget to double check that the steps add up to give you the overall equation. If they don't, it can't be right. (The steps add up fine in this example — I've just checked. Phew.)

Suggesting a mechanism

In the exams, you won't always be given a selection of possible mechanisms and asked to pick the right one. You could be given the overall equation and rate equation for a reaction and be asked to suggest a mechanism yourself. If this happens there are three rules you have to stick to:

- The rate-determining step of the reaction must fit with the rate equation.
- All of the equations in the mechanism must balance.
- The different steps of the reaction must add up to the overall equation.

Often there is more than one correct answer you could give, but as long as you stick to the rules above you should get the marks in the exam.

Exam Tip
If the reaction you're given involves a catalyst, you need to make sure that the catalyst is regenerated at the end.

Example

Nitrogen dioxide can react with fluorine to produce nitryl fluoride (NO_2F):

$$2NO_{2\,(g)} + F_{2\,(g)} \rightarrow 2NO_2F_{(g)}$$

The rate equation for this reaction is: rate = $k[NO_2][F_2]$. Suggest a possible two-step mechanism for this reaction. The first step is the slowest step.

Exam Tip
The rate-determining step won't necessarily be the first step in the reaction — but don't worry, you should be told which one is the slowest step.

The first step is the slowest step so this must be the rate-determining step. From the rate equation you can see that the rate determining step involves one molecule of NO_2 and one molecule of F_2. So the first step in the reaction must be:

$$NO_{2\,(g)} + F_{2\,(g)} \rightarrow ???$$

The second molecule of NO_2 isn't involved in the rate-determining step so it must be involved in the second step. This means that the second step in the reaction mechanism must be:

$$NO_{2\,(g)} + ??? \rightarrow ???$$

After that it's just a case of filling in the blanks, making sure that both equations balance and that you only end up with two molecules of NO_2F at the end. One possible solution is shown below:

$$NO_{2\,(g)} + F_{2\,(g)} \rightarrow NO_2F_{(g)} + F\bullet_{(g)}$$
$$NO_{2\,(g)} + F\bullet_{(g)} \rightarrow NO_2F_{(g)}$$

Tip: F• is a fluorine radical. Look back at Module 4: Section 1 for more on radicals.

In this example, the F• is an intermediate species — it is generated in the first step and consumed in the second step to leave you with the overall products of the reaction.

Another possible mechanism would be:

$$NO_{2\,(g)} + F_{2\,(g)} \rightarrow NO_2F_{2\,(g)}$$
$$NO_{2\,(g)} + NO_2F_{2\,(g)} \rightarrow 2NO_2F_{(g)}$$

This time NO_2F_2 is the intermediate species.

The correct mechanism is the first one, but in the exam you would get the marks for either answer because both answers fit the information that's given in the question.

Exam Tip
You could also have suggested a mechanism like this:

$$NO_2 + F_2 \rightarrow NO + F_2O$$
$$NO_2 + NO + F_2O \rightarrow 2NO_2F$$

But reactions happens when molecules collide, and it's very unlikely that 3 molecules would collide simultaneously. So try and avoid reaction mechanisms which involve more than two molecules reacting at a time.

Don't panic if you're asked to propose a mechanism in the exam. It sounds hard but as long as you follow the rules above you'll be just fine.

Exam Tip
These mechanism questions can feel quite tricky, but don't despair — once you've had a go at all these practice questions you'll feel a lot more confident tackling the ones that come up in the exams.

Practice Questions — Application

Q1 The rate-determining step for a reaction between two reactants (A and B) is $2A + B \rightarrow X + Y$. Predict the rate equation for this reaction.

Q2 The reaction $Br_{2(g)} + 2NO_{(g)} \rightarrow 2BrNO_{(g)}$ has a two step mechanism:

Step 1: $Br_{2(g)} + NO_{(g)} \rightarrow Br_2NO_{(g)}$

Step 2: $Br_2NO_{(g)} + NO_{(g)} \rightarrow 2BrNO_{(g)}$

Step 1 is the rate-determining step.
Write down the rate equation for this reaction.

Q3 The reaction $NO_{2(g)} + CO_{(g)} \rightarrow NO_{(g)} + CO_{2(g)}$ has a two-step mechanism:

Step 1: $2NO_{2(g)} \rightarrow NO_{(g)} + NO_{3(g)}$

Step 2: $NO_{3(g)} + CO_{(g)} \rightarrow NO_{2(g)} + CO_{2(g)}$

The rate equation for this reaction is rate = $k[NO_2]^2$.

a) What is the rate-determining step of this reaction? Explain your answer.

b) A one-step mechanism was also proposed for this reaction. How can you tell that this reaction isn't a one-step mechanism?

Tip: Remember that you can use free radicals in possible reaction mechanisms.

Q4 Under certain conditions, two molecules of ozone gas (O_3) will decompose to give oxygen gas (O_2):

$$2O_{3(g)} \rightarrow 3O_{2(g)}$$

The rate equation for this reaction was found to be rate = $k[O_3]$. Suggest a possible two-step mechanism for this reaction, given that the first step is the rate-determining step.

Tip: Don't forget — catalysts affect the rate of a reaction so they can be included in the rate equations too.

Q5 In the presence of an iodide (I^-) catalyst, hydrogen peroxide decomposes to give oxygen and water, as shown below:

$$2H_2O_{2(aq)} \rightarrow 2H_2O_{(l)} + O_{2(g)}$$

The rate equation for this reaction is rate = $k[H_2O_2][I^-]$.
The first step is the rate-determining step.
Suggest a possible two-step mechanism for this reaction.

Figure 1: *Hydrogen peroxide decomposing in the presence of an iodide ion catalyst. The bubbles are oxygen gas forming.*

Practice Questions — Fact Recall

Q1 What is the rate-determining step of a chemical reaction?

Q2 A reaction is second order with respect to oxygen. How many molecules of oxygen are involved in the rate-determining step?

Q3 One molecule of a particular reactant is involved in the rate-determining step of a reaction. What is the order of reaction with respect to that reactant?

8. The Arrhenius Equation

Changing the temperature of a reaction changes the rate constant. There's a handy equation that links the rate constant to the temperature and the activation energy of the reaction. It's time to meet the Arrhenius equation...

Rate and temperature

You learnt in Module 3: Section 2 that increasing the temperature of a reaction will increase its rate. This is because, for a reaction to happen, the particles need to collide with each other, have enough energy to react (i.e. have at least the activation energy) and have the right orientation. Increasing the temperature gives the reactant particles more kinetic energy. This means the particles speed up, so they collide more often. Increasing the temperature also means more reactant particles will have the required activation energy for the reaction, so a greater proportion of the collisions will result in the reaction actually happening. In other words, increasing temperature increases the reaction rate.

According to the rate equation, reaction rate depends only on the rate constant and reactant concentrations:

$$\text{Rate} = k[\text{A}]^m[\text{B}]^n$$

Changing the temperature won't have any effect on the concentration of the reactants, so instead it must change the rate constant. The rate constant and the temperature are correlated so the rate constant only applies to a particular reaction at a certain temperature. At a higher temperature, the reaction will have a higher rate constant.

HOW SCIENCE WORKS

The Arrhenius equation

The **Arrhenius equation** (nasty-looking thing in the purple box) links the rate constant (k) with activation energy (E_a, the minimum amount of kinetic energy particles need to react) and temperature (T). This is probably the worst equation you're going to meet in A Level Chemistry. Luckily, it'll be on your data sheet in the exams, so you don't have to learn it off by heart. But you do need to know what all the different bits mean, and how it works.
Here it is:

$$k = Ae^{\frac{-E_a}{RT}}$$

Where:

k = rate constant
E_a = activation energy (J mol^{-1})
T = temperature (K)
R = gas constant (8.31 J K^{-1} mol^{-1})
A = the pre-exponential factor (another constant. The units are the same as the rate constant.)

You can use the Arrhenius equation to predict how the rate constant (and so the rate of a reaction) will change if you change certain parameters, such as the activation energy or the temperature of the reaction.

Learning Objectives:

- Be able to give a qualitative explanation of the effect of temperature change on the rate of a reaction and hence the rate constant.
- Know that the exponential relationship between the rate constant, k, and temperature, T, is given by the Arrhenius equation, $k = Ae^{\frac{-E_a}{RT}}$.
- Be able to determine E_a and A graphically using the equation $\ln k = \frac{-E_a}{RT} + \ln A$ derived from the Arrhenius equation.

Specification Reference 5.1.1

Tip: The higher the rate constant, the faster the rate.

Tip: The Arrhenius equation is an exponential relationship. The 'e' is the e^x button on your calculator.

Exam Tip
Always double-check the units of any values you're given in the exams, as you may need to convert them before you use them in the Arrhenius equation. Temperature needs to be in kelvin, and the activation energy needs to be in joules per mole.

The rate constant and activation energy

As the activation energy, E_a, gets bigger, k gets smaller. You can test this out by trying different numbers for E_a in the equation... ahh go on, have a go.

Examples — Maths Skills

If you increase the activation energy, then this fraction becomes a larger, more negative number...

$$k = Ae^{\frac{-E_a}{RT}}$$

...which results in the value of the exponential becoming smaller, and so k also gets smaller.

If you decrease the activation energy, then this fraction becomes a smaller, less negative number...

$$k = Ae^{\frac{-E_a}{RT}}$$

...which results in the value of the exponential becoming larger, and so k also increases.

So, a large E_a will mean a slow rate. This makes sense when you think about it. If a reaction has a high activation energy, then not many of the reactant particles will have enough energy to react. So only a few of the collisions will result in the reaction actually happening, and the rate will be slow.

The rate constant and temperature

The equation also shows that as the temperature rises, k increases.

Examples — Maths Skills

If you increase the temperature, then this fraction becomes a smaller, less negative number...

$$k = Ae^{\frac{-E_a}{RT}}$$

...which results in the value of the exponential increasing, and so k increases.

If you decrease the temperature, then this fraction becomes a larger, more negative number...

$$k = Ae^{\frac{-E_a}{RT}}$$

...which results in the value of the exponential becoming smaller, and so k also decreases.

The temperature dependence makes sense too. Higher temperatures mean reactant particles move around faster and with more energy, so they're more likely to collide and more likely to collide with at least the activation energy, so the reaction rate increases.

Rearranging the Arrhenius equation

Putting the Arrhenius equation into logarithmic form makes it a bit easier to use.

Example — Maths Skills

- The exponential form of the Arrhenius equation is:

$$k = Ae^{\frac{-E_a}{RT}}$$

- If you take the natural logarithm of each side of this equation you get:

$$\ln(k) = \ln(Ae^{\frac{-E_a}{RT}})$$

Tip: e^{-x} is the same as '$1 \div e^x$', so as x gets bigger, e^{-x} gets smaller.

Tip: The term $e^{-E_a/RT}$ is called the exponential.

Tip: Increasing A will also increase the rate constant. R, the gas constant, never changes.

Tip: R, the gas constant, is a defined physical constant and never changes. By contrast, even though k and A are called constants, they are only constant for a particular reaction under certain conditions.

***Figure 1:** Svante Arrhenius, the chemist who came up with the Arrhenius equation.*

- The logarithm of two numbers that are multiplied together is equal to the sum of their logs:

$$= \ln(A) + \ln(e^{\frac{-E_a}{RT}})$$

- $\ln(x)$ and e^x are inverses of each other, so $\ln(e^x) = x$. Therefore,

$$\ln k = \frac{-E_a}{RT} + \ln A$$

Tip: Here, you can use the log rule that log (AB) = log A + log B. There's more about log rules in the Maths Skills section on page 552.

Tip: There's a handy 'ln' button on your calculator that you can use for finding the natural logarithm of a number.

Arrhenius plots

You can use the logarithmic form of the Arrhenius equation to create an **Arrhenius plot** by plotting $\ln k$ against $\frac{1}{T}$. This will produce a graph with a gradient of $\frac{-E_a}{R}$ and a y-intercept of $\ln A$. So once you've plotted the graph, you can find both the activation energy and the pre-exponential factor.

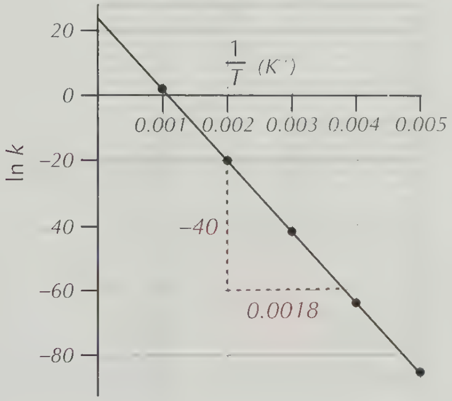
Tip: The logarithmic version of the Arrhenius equation,

$$\ln(k) = \frac{-E_a}{RT} + \ln A$$

is in the form $y = mx + c$, the equation for a straight-line graph.

Example — **Maths Skills**

The graph below shows an Arrhenius plot for the decomposition of hydrogen iodide (an overall second order reaction).
Calculate the activation energy and the pre-exponential factor for this reaction. $R = 8.31$ J K⁻¹ mol⁻¹.



- To find the value of E_a, find the gradient of the line of best fit from the Arrhenius plot:

  The gradient, $\frac{-E_a}{R} = \frac{-40}{0.0018} = -22\,222...$

  Now rearrange the equation $\frac{-E_a}{R} = -22\,222...$ to find the value of E_a:

  $E_a = -(-22\,222... \times R) = -(-22\,222... \times 8.31)$

  $= 184\,666...$ J mol⁻¹ = **185 kJ mol⁻¹**

- The value of $\ln A$ is found from the y-intercept:

  $\ln A = 24$

  So, $A = e^{24} = \mathbf{3 \times 10^{10}}$ **dm³ mol⁻¹ s⁻¹**

Exam Tip
E_a should always be a positive answer, so if you get a negative result, check your calculation to see where you've slipped up.

Tip: The value for A might vary a bit depending on whether you calculate it from the intercept or by substituting values into the logarithmic form of the Arrhenius equation. As long as they're in the same order of magnitude (raised to the same power of ten), then you don't need to worry.

Tip: If the axes are drawn so that you can't find the y-intercept, then you have to find A by substituting values into the logarithmic form of the Arrhenius equation.

- You could also find A by substituting values back into the logarithmic form of the Arrhenius equation now that you know E_a. You can use any data point from your graph to give you a value for k and T.

When $\ln k = -20$, $\frac{1}{T} = 0.002$

So $-20 = \frac{-184\,666...}{8.31} \times 0.002 + \ln A$

$\ln A = -20 + 44.4... = 24.4...$

$A = e^{24.4...} =$ $\mathbf{4 \times 10^{10}\ dm^3\ mol^{-1}\ s^{-1}}$

You can use the value of $\ln A$ calculated by substitution to check the value you obtained from the intercept. Here, they're both very similar (24.0 and 24.4), so both calculations have been done correctly.

Exam Tip
You'll be given the Arrhenius equation in the exam. It's:

$$k = Ae^{\frac{-E_a}{RT}}$$

Practice Questions — Application

Q1 Two reactions, reaction A and reaction B, are carried out at a temperature of 30 °C. Reaction A has an activation energy of 141.9 kJ mol^{-1}, and Reaction B has an activation energy of 132.9 kJ mol^{-1}.

a) Predict which reaction will have a larger rate constant. Explain your answer using the Arrhenius equation.

b) Reaction A is carried out again using the same concentration of reactants as before, but this time at a temperature of 45 °C. Predict whether this reaction will occur at a faster or slower rate than before, using the Arrhenius equation to explain your answer.

Tip: Before you draw the graph in Question 2, you'll have to work out $1/T$ and $\ln k$ at each point.

Q2 The table below shows how the rate constant of the following second order reaction changes with temperature:

$$H_2 + I_2 \rightarrow 2HI$$

Temperature / K	k / dm^3 mol^{-1} s^{-1}
280	1.25×10^{21}
300	1.79×10^{19}
320	1.38×10^{17}
340	6.34×10^{14}
360	1.91×10^{-14}
380	4.02×10^{-13}

a) Use the data to draw an Arrhenius plot.

b) Calculate the activation energy, E_a, for this reaction.

c) Calculate the pre-exponential factor, A, for this reaction.

Practice Questions — Fact Recall

Q1 Define each of the following terms in the Arrhenius equation, and state their units:

a) k b) E_a c) T d) A

Q2 Write the logarithmic form of the Arrhenius equation.

Q3 What is the significance of the gradient of the line given by a plot of $\ln k$ against $1/T$?

Section Summary

Make sure you know...

- That reaction rate is the change in the amount of reactants or products per unit time.
- The techniques and procedures used to investigate reaction rates, such as measuring volumes of gases or using colorimetry.
- How to convert data collected from continuous monitoring experiments into concentration-time data.
- How to work out reaction rates from concentration-time graphs.
- How to measure the initial rate of a reaction using the initial rates method.
- How to measure the initial rate of a reaction using a clock reaction.
- That reaction orders tell you how a reactant's concentration affects the rate of reaction.
- That the overall order of a reaction is the sum of the orders of all the reactants.
- How to use the initial rates method to work out reaction orders.
- How to deduce reaction orders from rate-concentration and concentration-time graphs.
- That the rate equation for the reaction A + B → C + D is rate = $k[\mathrm{A}]^m[\mathrm{B}]^n$.
- What each of the terms in the rate equation means.
- How to use the rate equation to predict the rate of a reaction.
- How to calculate the rate constant and its units, using the rate equation and experimental data.
- How to calculate the rate constant of a first order reaction from a rate-concentration graph.
- That the half-life of a reaction is the time taken for the amount of reactant to halve.
- How to deduce half-lives from concentration-time graphs.
- That the half-lives of first order reactions don't vary with concentration (the half-life is constant).
- How to find the rate constant of a first order reaction from the half-life.
- That the rate-determining step is the slowest step in a reaction mechanism.
- How to use the rate equation to determine which step in a reaction is the rate-determining step.
- How to propose a reaction mechanism from the rate equation and the overall equation for a reaction.
- That the rate constant, k, is always the same for a certain reaction at a particular temperature.
- That the Arrhenius equation links the rate constant to the activation energy and the temperature.
- That increasing the temperature increases the rate constant.
- That the Arrhenius equation can be rearranged into a logarithmic form, $\ln k = \ln A - E_a/RT$
- That the gradient of a graph of $1/T$ against $\ln k$ gives a straight line graph where the gradient is equal to $-E_a/R$, and the y-intercept is equivalent to $\ln A$.

Exam-style Questions

1 Increasing the value of which of the following variables will result in a decrease in rate, given that $k = Ae^{\frac{-E_a}{RT}}$?

A The Arrhenius constant.

B The temperature.

C The activation energy.

D The pressure.

(1 mark)

2 A reaction, A + B → C, is first order with respect to A and second order with respect to B. When [A] = 0.426 mol dm^{-3} and [B] = 0.775 mol dm^{-3}, the rate of the reaction is 0.00238 mol dm^{-3} s^{-1}. What is the rate constant?

A 0.00930 mol^{-2} dm^6 s^{-1}

B 0.00721 mol^{-1} dm^3 s^{-1}

C 0.00360 mol^{-1} dm^3 s^{-1}

D 0.00169 mol^{-2} dm^6 s^{-1}

(1 mark)

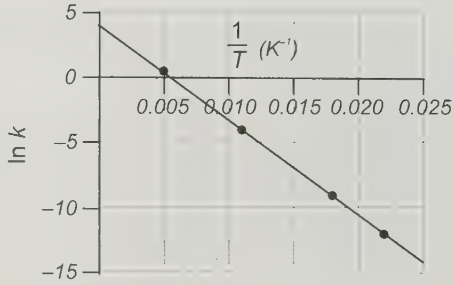
3 What is the pre-exponential factor, A, of the first order reaction in the Arrhenius plot on the right, given that the logarithmic form of the Arrhenius equation is $\ln k = \frac{-E_a}{RT} + \ln A$?

A 1.38 s^{-1}

B 4.0 s^{-1}

C 0.60 s^{-1}

D 54.6 s^{-1}



(1 mark)

4 Which of these experiments uses a continuous monitoring method?

A Measuring the time taken for 50 cm^3 of a gas to be produced at varying concentrations of one of the reactants.

B Measuring the pH of a reaction every 10 seconds from the start of the reaction until the time when the pH no longer changes.

C Measuring the time taken for a reaction that produces a gas to stop bubbling.

D Measuring how long it takes for a reaction mixture where a precipitate forms to go cloudy.

(1 mark)

5 Under certain conditions the following reaction occurs between nitrogen monoxide (NO) and hydrogen (H_2):

$$2NO_{(g)} + 2H_{2(g)} \rightarrow N_{2(g)} + 2H_2O_{(g)}$$

The table below shows the results of a series of initial rate experiments for this reaction.

Experiment	[NO] (mol dm^{-3})	[H_2](mol dm^{-3})	Initial rate (mol dm^{-3} s^{-1})
1	3.0×10^{-3}	6.0×10^{-3}	4.50×10^{-3}
2	3.0×10^{-3}	3.0×10^{-3}	2.25×10^{-3}
3	6.0×10^{-3}	1.5×10^{-3}	4.50×10^{-3}

(a) Determine the orders of reaction with respect to NO and H_2.

(2 marks)

(b) Write out the rate equation for this reaction.

(1 mark)

(c) Using the data above, calculate the rate constant (*k*) for this reaction and give its units.

(3 marks)

(d) What would the rate of reaction be if 4.5×10^{-3} mol dm^{-3} NO were mixed with 2.5×10^{-3} mol dm^{-3} H_2 under the same conditions as the experiment above?

(2 marks)

(e) (i) Using the rate equation, explain why a one-step mechanism is not possible for this reaction.

(2 marks)

(ii) Suggest a possible two step mechanism for this reaction. The first step is the slowest step.

(2 marks)

6 The table below shows how the rate constant, *k*, varies with temperature for the second order reaction:

$$CF_3Cl + Cl\bullet \rightarrow \bullet CF_3 + Cl_2$$

Temperature / °C	50	100	150	250	300
k / $mol^{-1}\,dm^3\,s^{-1}$	1.96×10^{-31}	1.36×10^{-28}	2.01×10^{-26}	2.50×10^{-23}	3.47×10^{-22}

(a) Draw an Arrhenius plot of 1/*T* against ln *k*.

(5 marks)

(b) Use the equation; $\ln k = \frac{-E_a}{RT} + \ln A$, to find:

(i) The activation energy, E_a, of the reaction.

(2 marks)

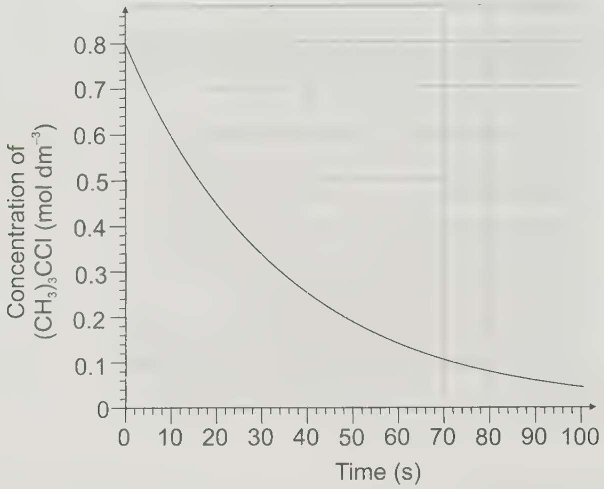
(ii) The pre-exponential factor, *A*, of the reaction.

(2 marks)

7 Under certain conditions, 2-chloro-2-methylpropane, $(CH_3)_3CCl$, will react with hydroxide ions as shown below:

$$(CH_3)_3CCl_{(aq)} + OH^-_{(aq)} \rightarrow (CH_3)_3COH_{(aq)} + Cl^-_{(aq)}$$

The reaction is zero order with respect to hydroxide ions. The graph below shows how the concentration of $(CH_3)_3CCl$ changes over time:



(a) **(i)** Given that the overall reaction is either zero or first order, what is the order of reaction with respect to $(CH_3)_3CCl$?

(1 mark)

(ii) Sketch a graph to show the shape of the rate-concentration graph for this reaction with respect to the concentration of $(CH_3)_3CCl$.

(1 mark)

(b) Write a rate equation for this reaction.

(1 mark)

(c) Calculate the rate of the reaction after:

(i) 20 seconds

(1 mark)

(ii) 40 seconds

(1 mark)

(d) What is the half-life of the reaction?

(1 mark)

(e) Find the rate constant, *k*, for this reaction.

(1 mark)

(f) Use your value of the rate constant to predict the rate of the reaction when the concentration of 2-chloro-2-methylpropane is 1.35 mol dm^{-3} and the concentration of hydroxide ions is 0.725 mol dm^{-3}.

(1 mark)

(g) Given that this reaction occurs in two steps, and the first step is the rate-determining step, predict a mechanism for this reaction.

(2 marks)

Module 5 Section 2: Equilibrium

1. The Equilibrium Constant

Hopefully you should remember a bit about reversible reactions and equilibrium constants from Module 3: Section 2. Now you'll need to learn a bit more detail. But first, a quick recap of dynamic equilibrium.

Learning Objectives:

- Be able to calculate K_c, or related quantities, including determination of units.
- Be able to calculate quantities present at equilibrium, given appropriate data.
- Be able to describe the techniques and procedures used to determine quantities present at equilibrium.
- Be able to deduce expressions for K_c for homogeneous and heterogeneous equilibria.

Specification Reference 5.1.2

Dynamic equilibrium

When a reversible reaction reaches dynamic equilibrium, the forward and reverse reactions are going at the same rate and there's no overall change in the concentrations of the reactants and products. A dynamic equilibrium can only happen in a **closed system** (a system where nothing can get in or out) at a constant temperature. Equilibria can be set up in physical systems and chemical systems:

Examples

Physical Systems

When liquid bromine is shaken in a closed flask, some of it changes to orange bromine gas. After a while, equilibrium is reached — bromine liquid is still changing to bromine gas and bromine gas is still changing to bromine liquid, but they are changing at the same rate.

$$Br_{2(l)} \rightleftharpoons Br_{2(g)}$$

Chemical Systems

If hydrogen gas and iodine gas are mixed together in a closed flask, hydrogen iodide is formed.

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$

Imagine that 1.0 mole of hydrogen gas is mixed with 1.0 mole of iodine gas at a constant temperature of 640 K. When this mixture reaches equilibrium, there will be 1.6 moles of hydrogen iodide and 0.2 moles of both hydrogen gas and iodine gas. No matter how long you leave them at this temperature, the equilibrium amounts never change. As with the physical system, it's all a matter of the forward and backward rates being equal.

Figure 1: A flask containing bromine at equilibrium.

The equilibrium constant, K_c

You'll have encountered the expression for the **equilibrium constant**, K_c, on page 193 but you'll be using it a lot over the next couple of pages so it never hurts to recap:

The lower-case letters a, b, d and e are the number of moles of each substance in the equation.

For the general reaction $aA + bB \rightleftharpoons dD + eE$:

$$K_c = \frac{[D]^d[E]^e}{[A]^a[B]^b}$$

The square brackets, [ ], mean concentration in mol dm^{-3}.

The products go on the top line and the reactants go on the bottom line.

Tip: The superscript numbers look like the orders of reaction that you saw in rate equations. But they're not — they're the numbers of moles in the equation.

Calculating K_c

If you know the equilibrium concentrations, just bung them in your expression. Then with a bit of help from the old calculator, you can work out the value of K_c. The units are a bit trickier though — they vary, so you have to work them out after each calculation.

Tip: If K_c is large, at equilibrium there will be lots of product and not much reactant. If K_c is small, it's the other way around — at equilibrium there'll be lots of reactant but not much product.

Example — Maths Skills

Calculate K_c, including units, for the reaction:

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$$

At 298 K, the equilibrium concentrations are:

$[N_2O_4] = 4.17 \times 10^{-2}$ mol dm^{-3}, $[NO_2] = 1.41 \times 10^{-3}$ mol dm^{-3}

Just stick the concentrations into the expression for K_c:

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} = \frac{(0.00141)^2}{0.0417} = 4.77 \times 10^{-5}$$

Now work out the units for the equilibrium constant by substituting the units for each component into the expression for K_c:

$$K_c = \frac{(\text{mol dm}^{-3})\cancel{(\text{mol dm}^{-3})}}{\cancel{\text{mol dm}^{-3}}} = \text{mol dm}^{-3}$$

So K_c = **4.77×10^{-5} mol dm^{-3}**

Exam Tip

In exam questions on K_c you'll often be told the temperature. You don't need this value for your calculation — it's just so you know the temperature is constant.

Tip: K_c has units of mol dm^{-3} in this example but this won't always be the case, so always work the units out — there's often a mark for giving the correct units in the exam.

You might have to figure out some of the equilibrium concentrations before you can find K_c. To do this follow these steps:

Step 1: Find out how many moles of each reactant and product there are at equilibrium.
(You'll usually be given the number of moles at equilibrium for one of the reactants. You can then use the balanced reaction equation to work out the number of moles of all the others.)

Step 2: Calculate the molar concentrations of each reactant and product by dividing each number of moles by the volume of the reaction.
(You'll be told the volume in the question but you may have to convert it into different units. To work out molar concentrations you need the volume to be in dm^3.)

Tip: The molar concentration is just the concentration in mol dm^{-3}.

Once you've done this you're ready to substitute your values into the expression for K_c and calculate it.

Example — Maths Skills

0.20 moles of phosphorus(V) chloride decomposes at 600 K in a vessel of 5.00 dm^3. The equilibrium mixture is found to contain 0.080 moles of chlorine. Write the expression for K_c and calculate its value, including units.

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$$

1. Find out how many moles of PCl_5 and PCl_3 there are at equilibrium:
   - The equation tells you that when 1 mole of PCl_5 decomposes, 1 mole of PCl_3 and 1 mole of Cl_2 are formed.
   - So if 0.080 moles of chlorine are produced at equilibrium, then there will be 0.080 moles of PCl_3 as well.

Exam Tip

For long wordy questions like this it can help to highlight any important bits of information before you start — e.g. any concentrations or volumes you're given.

- 0.080 moles of PCl_5 must have decomposed to form 0.080 moles of Cl_2 and PCl_3, so there will be 0.12 moles of PCl_5 left at equilibrium (0.20 – 0.080 = 0.12).

2. Divide each number of moles by the volume of the flask to give the molar concentrations:

$$[PCl_3] = [Cl_2] = \frac{0.080}{5.00} = 0.016 \text{ mol dm}^{-3}$$

$$[PCl_5] = \frac{0.12}{5.00} = 0.024 \text{ mol dm}^{-3}$$

3. Put the concentrations in the expression for K_c and calculate it:

$$K_c = \frac{[PCl_3]\,[Cl_2]}{[PCl_5]} = \frac{[0.016]\,[0.016]}{[0.024]} = 0.011$$

4. Now find the units of K_c:

$$K_c = \frac{(\text{mol dm}^{-3})\cancel{(\text{mol dm}^{-3})}}{\cancel{\text{mol dm}^{-3}}} = \text{mol dm}^{-3}$$

So K_c = **0.011 mol dm^{-3}**

Exam Tip
You may be asked to calculate the molar amounts of some substances in an earlier part of the question — if this happens you can reuse your answers to find K_c. Handy.

Exam Tip
When you're writing expressions for K_c make sure you use [square brackets]. If you use (rounded brackets) you won't get the marks.

Here's one more example.

Example **Maths Skills**

0.100 mol dm^{-3} Cu^{2+} ions are mixed with 0.300 mol dm^{-3} HCl to form the following equilibrium: $Cu^{2+}_{(aq)} + 4Cl^-_{(aq)} \rightleftharpoons [CuCl_4]^{2-}_{(aq)}$
At equilibrium, the concentration of $[CuCl_4]^{2-}_{(aq)}$ is x mol dm^{-3}.
Write an expression for K_c in terms of x.

From the equation, for every mole of $[CuCl_4]^{2-}_{(aq)}$ formed, you will lose 1 mole $Cu^{2+}_{(aq)}$ and 4 moles $Cl^-_{(aq)}$ from your initial reactant concentrations. So if x moles of $[CuCl_4]^{2-}_{(aq)}$ have formed, you will have lost x moles $Cu^{2+}_{(aq)}$ and $4x$ moles $Cl^-_{(aq)}$. So the equilibrium concentrations will be:

- $Cu^{2+}_{(aq)}$ = (initial $Cu^{2+}_{(aq)}$ concentration) – x
- $Cl^-_{(aq)}$ = (initial $Cl^-_{(aq)}$ concentration) – $4x$

You can use this information to construct a table:

Equilibrium component	$Cu^{2+}_{(aq)}$	$Cl^-_{(aq)}$	$[CuCl_4]^{2-}_{(aq)}$
Initial conc. (mol dm^{-3})	0.100	0.300	0
Equilibrium conc. (mol dm^{-3})	0.100 – x	0.300 – $4x$	x

From your equilibrium concentrations, you can see that:

$$K_c = \frac{[[CuCl_4]^{2-}]}{[Cu^{2+}]\,[Cl^-]^4} = \frac{x}{(0.100 - x)\,(0.300 - 4x)^4}$$

At 291 K, the equilibrium concentration of $[CuCl_4]^{2-}$ for the equilibrium shown above is 0.0637 mol dm^{-3}. Calculate K_c.

Substitute the concentration of $[CuCl_4]^{2-}$ at equilibrium for x:

$$x = 0.0637 \text{ mol dm}^{-3}\text{, so } K_c = \frac{0.0637}{(0.100 - 0.0637)\,(0.300 - 4 \times 0.0637)^4}$$

$$= \mathbf{4.20 \times 10^5 \text{ mol}^{-4} \text{ dm}^{12}}$$

Tip: The square brackets in $[CuCl_4]^{2-}_{(aq)}$ in this example show that the species is a complex ion — it has nothing to do with concentration.

Using K_c

If you know the value of K_c you can use it to find unknown equilibrium concentrations. Here's how you do it:

Step 1: Put all the values you know into the expression for K_c.

Step 2: Rearrange the equation and solve it to find the unknown values.

Tip: Equilibrium concentrations can be determined experimentally by measuring pH, if the equilibrium involves an acid or base (see page 356). A colorimeter can be used to determine equilibrium concentrations if the equilibrium species are coloured (see page 290).

Example **Maths Skills**

When ethanoic acid was allowed to reach equilibrium with ethanol at 25 °C, it was found that the equilibrium mixture contained 2.0 mol dm^{-3} ethanoic acid and 3.5 mol dm^{-3} ethanol. The K_c of the equilibrium is 4.0 at 25 °C. What are the concentrations of the other components?

$$\mathbf{CH_3COOH_{(l)} + C_2H_5OH_{(l)} \rightleftharpoons CH_3COOC_2H_{5(l)} + H_2O_{(l)}}$$

1. Put all the values you know in the K_c expression:

$$K_c = \frac{[CH_3COOC_2H_5]\,[H_2O]}{[CH_3COOH]\,[C_2H_5OH]} \quad \text{so} \quad 4.0 = \frac{[CH_3COOC_2H_5]\,[H_2O]}{2.0 \times 3.5}$$

2. Rearranging this gives:

$$[CH_3COOC_2H_5][H_2O] = 4.0 \times 2.0 \times 3.5 = 28.0$$

From the equation, you know that $[CH_3COOC_2H_5] = [H_2O]$, so:

$$[CH_3COOC_2H_5] = [H_2O] = \sqrt{28} = 5.3 \text{ mol dm}^{-3}$$

The concentration of $CH_3COOC_2H_5$ and H_2O is **5.3 mol dm^{-3}**.

Tip: The units of concentration should always be mol dm^{-3}. If your answer doesn't give you this then go back and check your calculation to see where you've gone wrong.

Calculating K_c for heterogeneous equilibria

If all the reactants and products in a reaction are in the same state (e.g. they're all gases, or all in solution) then the reaction is homogeneous. All the calculations in this topic so far have involved homogeneous equilibria. But if the reactants and products in a reaction are in different states the reaction is heterogeneous. A heterogeneous reaction can change what you put in the equilibrium constant expression. The rule is:

- If the mixture is homogeneous, all the reactants and products are put into the expression for the equilibrium constant.
- If the mixture is heterogeneous, only gases and aqueous substances go into the expression for the equilibrium constant (any solids or liquids get left out).

Example **Maths Skills**

Write an expression for the equilibrium constant of the following reaction:

$$\mathbf{Cu_{(s)} + 2Ag^+_{(aq)} \rightleftharpoons Cu^{2+}_{(aq)} + 2Ag_{(s)}}$$

The reactants and products are a mixture of aqueous and solid. So the reaction is heterogeneous. Only the aqueous substances go into the equilibrium constant.

$$\text{So } \boldsymbol{K_c} = \frac{[\mathbf{Cu^{2+}}]}{[\mathbf{Ag^+}]^2}$$

At a certain temperature, there are 0.431 mol dm^{-3} Ag^+ and 0.193 mol dm^{-3} Cu^{2+} at equilibrium. Calculate K_c and give its units.

$$K_c = \frac{[Cu^{2+}]}{[Ag^+]^2} = \frac{0.193}{(0.431)^2} = 1.04$$

The units are $\frac{\cancel{(\text{mol dm}^{-3})}}{(\text{mol dm}^{-3})^{\cancel{2}}} = \frac{1}{\text{mol dm}^{-3}} = \text{mol}^{-1}\,\text{dm}^3$

So K_c = **1.04 mol^{-1} dm^3**

Tip: If the units end up as (1 / mol dm^{-3}), you write that as mol^{-1} dm^3.

Practice Questions — Application

Q1 The following equilibrium exists under certain conditions:

$$C_2H_{4(g)} + H_2O_{(g)} \rightleftharpoons C_2H_5OH_{(g)}$$

a) Write out the expression for the equilibrium constant, K_c, for this reaction.

5.00 moles of C_2H_5OH was placed in a container and allowed to reach equilibrium. At a certain temperature and pressure the equilibrium mixture was found to contain 1.85 moles of C_2H_4, and have a total volume of 15.0 dm^3.

b) Determine the number of moles of each substance at equilibrium.

c) Calculate the molar concentrations (in mol dm^{-3}) of all the reagents at equilibrium.

d) Calculate K_c for this equilibrium.

At a different temperature and pressure, the value of K_c = 3.8 and the equilibrium mixture contained 0.80 mol dm^{-3} C_2H_5OH.

e) Determine the equilibrium concentrations of C_2H_4 and H_2O under these conditions.

Tip: Don't forget — you need to work out the units of K_c too.

Q2 Under certain conditions the following equilibrium is established:

$$2SO_{2(g)} + O_{2\,(g)} \rightleftharpoons 2SO_{3\,(g)}$$

a) Write out an expression for K_c for this reaction.

At a certain temperature, the equilibrium concentrations for the three reagents were found to be:

SO_2 = 0.250 mol dm^{-3} O_2 = 0.180 mol dm^{-3} SO_3 = 0.360 mol dm^{-3}

b) Calculate K_c for this equilibrium.

c) If all other conditions (including the concentrations of O_2 and SO_3) were to stay the same, what would the equilibrium concentration of SO_2 have to be for K_c to be 15?

Q3 250 cm^3 0.500 mol dm^{-3} iron(II) sulfate solution is added to 250 cm^3 0.500 mol dm^{-3} silver(I) nitrate at 298 K to set up the following equilibrium reaction:

$$Fe^{2+}_{(aq)} + Ag^{+}_{(aq)} \rightleftharpoons Fe^{3+}_{(aq)} + Ag_{(s)}$$

Once the solution has reached equilibrium, a sample is taken and titrated to calculate the concentration of Fe^{2+} ions. Given that at equilibrium, $[Fe^{2+}_{(aq)}] = 0.0844$ mol dm^{-3}, calculate K_c.

Practice Questions — Fact Recall

Q1 Explain what is meant by the term 'dynamic equilibrium'.

Q2 Describe the conditions that are needed for a dynamic equilibrium to be established.

Q3 Write out an expression for K_c for the general reaction:

$$aA + bB \rightleftharpoons dD + eE$$

Q4 What are the units of K_c?

2. Gas Equilibria

When you're dealing with equilibrium reactions involving gases, it's easier to think in terms of pressure than in terms of concentrations. A gaseous equilibrium system will have a total pressure, but there will also be individual pressures for each of the individual gases. These are called partial pressures.

Learning Objectives:

- Be able to use the terms partial pressure and mole fraction.
- Be able to calculate K_p, or related quantities, including determination of units.
- Be able to deduce expressions for K_p for homogeneous and heterogeneous equilibria.

Specification Reference 5.1.2

Partial pressures

In a mixture of gases, each individual gas exerts its own pressure — this is called its **partial pressure**.

Example

The reaction between hydrogen and iodine vapour is an example of a gaseous equilibrium reaction.

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$

In this reaction, the total pressure can be expressed as:

Total pressure = $p(H_2) + p(I_2) + p(HI)$

In the example above, hydrogen, iodine and hydrogen iodide are all gases and will all exert a pressure on the system. The size of the pressure exerted by each gas doesn't have to be the same. Partial pressures are often written as $p(X)$ — this just means the partial pressure of X. The partial pressure of X depends on the number of moles of X present.

The total pressure of a gas mixture is the sum of all the partial pressures of the individual gases. You can put this fact into use when dealing with pressure calculations, such as the one below.

Figure 1: John Dalton, the English chemist, who came up with the theory that the total pressure of a mixture of gases is equal to the sum of the partial pressures of the gases in the mixture. This theory is also known as Dalton's Law.

Example — Maths Skills

When 3.00 moles of the gas PCl_5 is heated, it decomposes into PCl_3 and Cl_2:

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$$

In a sealed vessel at 500 K, the equilibrium mixture contains chlorine with a partial pressure of 263 kPa. If the total pressure of the mixture is 714 kPa, what is the partial pressure of PCl_5?

From the equation, you know that PCl_3 and Cl_2 are produced in equal amounts, so the partial pressures of these two gases are the same at equilibrium — they're both 263 kPa.

Total pressure = $p(PCl_5) + p(PCl_3) + p(Cl_2)$

$$714 = p(PCl_5) + 263 + 263$$

So the partial pressure of PCl_5 = 714 – 263 – 263 = **188 kPa**

Mole fractions

Partial pressures can be worked out from mole fractions. A '**mole fraction**' is just the proportion of a gas mixture that is a made up of a particular gas. So if you have four moles of gas in total and two of them are gas A, the mole fraction of gas A is 0.5. There are two formulas you need on the next page.

Exam Tip
You won't be given these equations in the exam — make sure you learn them off by heart so you can handle any K_p calculations the examiners could throw at you.

$$\text{Mole fraction of a gas in a mixture} = \frac{\text{number of moles of gas}}{\text{total number of moles of gas in the mixture}}$$

$$\text{Partial pressure of a gas in a mixture} = \text{mole fraction of gas} \times \text{total pressure of the mixture}$$

Example — **Maths Skills**

When 3.00 moles of PCl_5 is heated in a sealed vessel, the equilibrium mixture contains 1.75 moles of chlorine. If the total pressure of the mixture is 714 kPa, what is the partial pressure of PCl_5?

First, write out a chemical equation so you can see what's happening:

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$$

From the equation, PCl_3 and Cl_2 are produced in equal amounts, so there'll be 1.75 moles of PCl_3 too.

1.75 moles of PCl_5 must have decomposed, so (3.00 – 1.75) = 1.25 moles of PCl_5 must be left at equilibrium.

This means that the total number of moles of gas at equilibrium = 1.75 + 1.75 + 1.25 = 4.75.

So the mole fraction of $PCl_5 = \frac{1.25}{4.75} = 0.263...$

The partial pressure of PCl_5 = mole fraction × total pressure
= 0.263... × 714 = **188 kPa**

Tip: You need to use a balanced chemical equation when working out mole fractions — you have to take into account the ratio of the number of moles of each gas when working out the mole fraction of a particular reactant or product.

The gas equilibrium constant, K_p

K_p is the equilibrium constant for a reversible reaction where some, or all, of the reactants and products are gases. The expression for K_p is just like the one for K_c, except you use partial pressures instead of concentrations.

For the equilibrium
$aA_{(g)} + bB_{(g)} \rightleftharpoons dD_{(g)} + eE_{(g)}$

$$K_p = \frac{p(D)^d\, p(E)^e}{p(A)^a\, p(B)^b}$$

Tip: K_c and K_p work in pretty much exactly the same way — K_p is just specifically for gases.

Example

Write an expression for K_p for the following reaction.

$$O_{3(g)} + H_2O_{(g)} \rightleftharpoons H_{2(g)} + 2O_{2(g)}$$

There are two moles of O_2 in the balanced equation, so the partial pressure of O_2 needs to be raised to the power of 2.

$$K_p = \frac{p(O_2)^2 \times p(H_2)}{p(O_3) \times p(H_2O)}$$

The reactants go on the bottom of the expression.

The products go on the top of the expression.

Tip: Solid, liquid and aqueous substances don't appear in the expression for K_p. They also don't contribute to the total pressure of a system (see page 332).

Tip: Make sure your chemical equation is balanced — otherwise you'll get your expression for K_p wrong.

To calculate K_p you put the partial pressures in the expression. Then you work out the units like you did for K_c.

Example — Maths Skills

Calculate K_p for the decomposition of PCl_5 gas at 500 K. The partial pressures of each gas are:
$p(PCl_5) = 188$ kPa, $p(PCl_3) = 263$ kPa, $p(Cl_2) = 263$ kPa

Start by writing out a balanced chemical equation:
$PCl_{5\,(g)} \rightleftharpoons PCl_{3\,(g)} + Cl_{2\,(g)}$

Now, write an expression for K_p. Remember, the reactants go on the bottom of the expression, and the products go on the top.

$$K_p = \frac{p(Cl_2) \times p(PCl_2)}{p(PCl_5)}$$

Then just substitute in all the partial pressure values you were given in the question.

$$K_p = \frac{263 \times 263}{188} = 368$$

To find the units, substitute all the partial pressure units into your expression for K_p, then cancel down as much as you can.

$$K_p = \frac{\cancel{kPa} \times kPa}{\cancel{kPa}} = kPa \qquad \text{So } K_p = \mathbf{368\ kPa}$$

Tip: If you're given an equation that contains a non-gaseous chemical, then don't include it in your equation for K_p. For example:
$H_2O_{(g)} + C_{(s)} \rightleftharpoons H_{2(g)} + CO_{(g)}$

$$K_p = \frac{p(H_2) \times p(CO)}{p(H_2O)}$$

C is not included in the expression for K_p because it's a solid — not a gas. There's more about this on the next page.

Tip: K_p is temperature dependent (see page 331). So, a particular value of K_p is only valid at a given temperature.

You might be given K_p for a reaction and have to use it to calculate equilibrium partial pressures.

Example — Maths Skills

An equilibrium exists between ethanoic acid monomers, CH_3COOH, and dimers, $(CH_3COOH)_2$. At 160 °C the K_p for the reaction

$$(CH_3COOH)_{2(g)} \rightleftharpoons 2CH_3COOH_{(g)}$$

is 180 kPa. At this temperature the partial pressure of the dimer, $(CH_3COOH)_2$, is 28.5 kPa. Calculate the partial pressure of the monomer in this equilibrium and state the total pressure exerted by the equilibrium mixture.

First, use the chemical equilibrium to write an expression for K_p:

$$K_p = \frac{p(CH_3COOH)^2}{p((CH_3COOH)_2)}$$

This rearranges to give: $p(CH_3COOH)^2 = K_p \times p((CH_3COOH)_2)$

$$= 180 \times 28.5 = 5130$$

$$p(CH_3COOH) = \sqrt{5130} = 71.6 \text{ kPa}$$

So the total pressure of the equilibrium mixture = 28.5 + 71.6 = **100 kPa**

K_p for heterogeneous equilibria

You met the idea of homogeneous and heterogeneous equilibria on page 324. Up until now we've only thought about K_p expressions for homogeneous equilibria. If you're writing an expression for K_p for a heterogeneous equilibrium, you don't include solids or liquids.

Example

Write an expression for K_p for the following reaction:

$$NH_4HS_{(s)} \rightleftharpoons NH_{3(g)} + H_2S_{(g)}$$

The equilibrium is heterogeneous — a solid decomposes to form two gases. Solids don't get included in K_p, so **$K_p = p(NH_3)\,p(H_2S)$**.

Tip: Being able to write balanced chemical equations is a really important skill in chemistry. It will help you solve loads of questions. Look back at page 66 for more details.

Tip: Remember — moles = mass ÷ M_r.

Practice Questions — Application

Q1 Ammonia gas is reacted with oxygen gas in a reversible reaction. The products are nitrogen gas and water vapour.

a) Write out a balanced chemical equation for this reaction.

b) Write out an expression for the total pressure of the system.

c) $p(O_2) = 85$ kPa, $p(NH_3) = 42$ kPa, $p(N_2) = 21$ kPa, and $p(H_2O) = 12$ kPa.
Calculate the total pressure of the system.

d) What is the mole fraction of water vapour in the system?

Q2 A sealed container holds 4.00 g of helium gas (He) and 2.81 g of oxygen gas. Given that the total pressure of the container is 8.12 kPa, what is the partial pressure of oxygen?

Q3 The following equation shows the reaction between benzene and hydrogen to create cyclohexane:

$$C_6H_{6\,(g)} + 3H_{2\,(g)} \rightleftharpoons C_6H_{12\,(g)}$$

a) Write an equation for K_p for the reaction above.

b) At equilibrium, the partial pressures of the three gases are all equal. Given that $K_p = 4.80 \times 10^{-13}$ kPa^{-3}, what is the partial pressure of hydrogen?

Q4 When 24.32 moles of hydrogen fluoride are heated in a sealed vessel, the equilibrium mixture contains 9.340 moles of fluorine gas.

a) If the total pressure of the mixture is 2313 kPa, what is the partial pressure of hydrogen?

b) Calculate the gas equilibrium constant for this reaction.

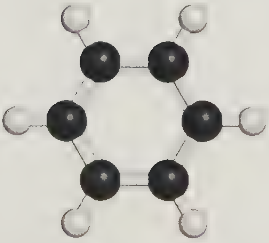


Figure 2: A molecular model of benzene (C_6H_6). In the hydrogenation of benzene, hydrogen is added to the aromatic ring to create a saturated alkane — cyclohexane.

Practice Questions — Fact Recall

Q1 What is meant by the term 'partial pressure'?

Q2 What equation links the mole fraction of a gas, the number of moles of that gas and the total number of moles of gas in a mixture?

Q3 What is K_p?

Q4 Write an expression for K_p for the equation: $aA_{(g)} + bB_{(g)} \rightleftharpoons dD_{(g)} + eE_{(g)}$.

3. Changing the Equilibrium

The position of equilibrium for a reaction can change if conditions change, but not all changes in conditions result in a change in the value of K_c.

Changing the position of equilibrium

If you change the concentration, pressure or temperature of a reversible reaction, you're going to alter the position of equilibrium. This just means you'll end up with different amounts of reactants and products at equilibrium.

- If the position of equilibrium moves to the left, you'll get more reactants.

$$H_{2(g)} + I_{2(g)} \leftrightharpoons 2HI_{(g)}$$

- If the position of equilibrium moves to the right, you'll get more products.

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$

There's a rule that lets you predict how the position of equilibrium will change if a condition changes. This rule is known as **Le Chatelier's Principle**:

> Le Chatelier's Principle: If there's a change in concentration, pressure or temperature, the equilibrium will move to help counteract the change.

So, basically, if you raise the temperature, the position of equilibrium will shift to try to cool things down. And if you raise the pressure or concentration, the position of equilibrium will shift to try to reduce it. Although changes in temperature and changes in concentration both affect the position of the equilibrium, only changing the temperature affects the value of K_c. The size of the equilibrium constant tells you where the equilibrium lies:

- The larger the value of K_c, the further to the right the equilibrium lies.
- The smaller the value of K_c, the further to the left the equilibrium lies.

Changing the temperature

If you increase the temperature, you add heat. The equilibrium shifts in the **endothermic** (positive ΔH) direction to absorb the heat. Decreasing the temperature removes heat energy. The equilibrium shifts in the **exothermic** (negative ΔH) direction to try to replace the heat. If the forward reaction's endothermic, the reverse reaction will be exothermic, and vice versa. If the change means more product is formed, K_c will rise. If it means less product is formed, then K_c will decrease. So, changing the temperature alters the position of equilibrium and therefore the value of the equilibrium constant.

Examples

The reaction below is exothermic in the forward direction:

Exothermic →

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)} \qquad \Delta H = -197 \text{ kJ mol}^{-1}$$

← *Endothermic*

Learning Objectives:

- Be able to explain the qualitative effect on equilibrium constants of changing temperature for exothermic and endothermic reactions.
- Be able to explain the constancy of equilibrium constants with changes in concentration, pressure or in the presence of a catalyst.
- Be able to explain how an equilibrium constant controls the position of equilibrium on changing concentration, pressure and temperature.

Specification Reference 5.1.2

Tip: You've come across Le Chatelier's Principle before — on pages 188-190.

Figure 1: Henri Le Chatelier.

Tip: The ΔH values given for reversible reactions show the ΔH of the forward reaction.

Tip: If the temperature decreases the opposite happens — for reactions that are exothermic in the forward direction K_c will increase and for reactions that are endothermic in the forward direction K_c will decrease.

If you increase the temperature, the equilibrium shifts to the left (in the endothermic direction) to absorb some of the extra heat energy. This means that less product's formed so the concentration of product ($[SO_3]$) will be less.

$$K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$$

There's less product and more reactant, so the number on the top gets smaller and the number on the bottom gets bigger. This means K_c must have decreased.

The reaction below is endothermic in the forward direction:

$$\overset{\text{Endothermic} \longrightarrow}{CH_{4(g)} \rightleftharpoons 2H_{2(g)} + C_{(s)}} \qquad \Delta H = +90 \text{ kJ mol}^{-1}$$

$$\longleftarrow \text{Exothermic}$$

This time increasing the temperature shifts the equilibrium to the right. This means more product's formed, so K_c increases.

Changing the concentration

Tip: Don't get confused — the position of the equilibrium can change without affecting the value of K_c.

The value of the equilibrium constant, K_c, is fixed at a given temperature. So if the concentration of one thing in the equilibrium mixture changes then the concentrations of the others must change to keep the value of K_c the same.

Example

$$CH_3COOH_{(l)} + C_2H_5OH_{(l)} \rightleftharpoons CH_3COOC_2H_{5(l)} + H_2O_{(l)}$$

If you increase the concentration of CH_3COOH then the equilibrium will move to the right to get rid of some of the extra CH_3COOH — so more $CH_3COOC_2H_5$ and H_2O are produced. This keeps the equilibrium constant the same.

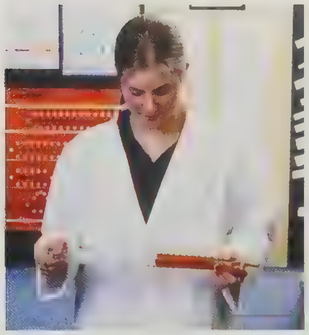


Figure 2a: *Equilibrium between $NO_{2(g)}$ (brown) and $N_2O_{4(l)}$ (colourless).*

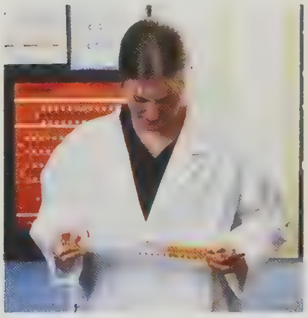


Figure 2b: *When pressure is applied the colour changes because the equilibrium shifts in favour of $N_2O_{4(l)}$.*

Changing the pressure

Changing the pressure only really affects equilibria involving gases. Increasing the pressure shifts the equilibrium to the side with fewer gas molecules — this reduces the pressure. Decreasing the pressure shifts the equilibrium to the side with more gas molecules. This raises the pressure again. K_p and K_c stay the same, no matter what you do to the pressure.

Example

The following equilibrium exists between nitrogen dioxide (NO_2) and nitrogen tetroxide (N_2O_4):

$$2NO_{2(g)} \rightleftharpoons N_2O_{4(g)}$$

There are 2 moles of gas on the left, but only 1 mole of gas on the right. So an increase in pressure would shift the equilibrium to the right.

This shift in equilibrium can be seen because NO_2 is a brown gas (see Figure 2a). If pressure is applied to the gas (e.g. in a syringe), the colour becomes paler (see Figure 2b). This is because the equilibrium has shifted to the right and some of the brown NO_2 has been converted to N_2O_4 which is colourless.

So, the equilibrium shifts to the right. However, the values of K_p and K_c stay the same.

Adding a catalyst

Catalysts have no effect on the position of equilibrium or on the value of K_c or K_p. This is because a catalyst will increase the rate of both the forward and backward reactions by the same amount. As a result, the equilibrium position will be the same as the uncatalysed reaction, but equilibrium will be reached faster. So catalysts can't increase yield (the amount of product produced) — but they do decrease the time taken to reach equilibrium.

Example

The Haber process is used to synthesise ammonia:

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

This reaction uses an iron catalyst. Adding the iron catalyst decreases the amount of time taken for this reaction to reach equilibrium, but it has no effect on the equilibrium position or on the value of K_p or K_c.

Exam Tip

Don't be thrown if a reaction you're given in the exam has a catalyst. Catalysts don't affect the equilibrium constants.

Practice Questions — Application

Q1 The following equilibrium is established under certain conditions:

$$2CHClF_{2(g)} \rightleftharpoons C_2F_{4(g)} + 2HCl_{(g)} \qquad \Delta H = +128 \text{ kJ mol}^{-1}$$

State and explain how you would expect the following to affect the value of K_c for this equilibrium:

a) Increasing the concentration of C_2F_4.

b) Increasing the temperature.

c) Adding a catalyst.

Q2 The value of K_c for the following equilibrium increases if the temperature is decreased:

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

a) Is the forward reaction endothermic or exothermic? Explain your answer.

b) How would decreasing the pressure of this reaction affect:

  (i) the position of equilibrium?

  (ii) the value of K_p?

Q3 The reaction below occurs between methane and steam:

$$CH_{4(g)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + 3H_{2(g)}$$

The forward reaction is endothermic.

a) How could you increase the value of K_p for this equilibrium?

b) How could you increase production of $H_{2(g)}$ without affecting the value of K_p?

Exam Tip

In the exam, make sure you read the question really carefully and pay attention to whether concentrations and temperatures are increasing or decreasing — one slip up could cause you trouble...

Practice Questions — Fact Recall

Q1 State Le Chatelier's principle.

Q2 How will increasing the temperature affect K_c if:

a) the forward reaction is endothermic?

b) the forward reaction is exothermic?

Q3 Explain why changing the concentration of a reagent does not affect K_c.

Q4 How does increasing the pressure of a reaction affect the value of K_p?

Q5 How does adding a catalyst affect an equilibrium?

Section Summary

Make sure you know...

- How to calculate K_c and its units from the equilibrium concentrations and molar ratios for a reaction.
- How to use K_c to find unknown equilibrium concentrations for a reaction.
- How to deduce expressions for K_c for homogeneous and heterogeneous equilibria.
- That partial pressure is the pressure an individual gas in a mixture exerts.
- That a mole fraction is the proportion of a gas mixture that is a made up of a particular gas.
- How to calculate K_p and its units from the equilibrium partial pressures for a reaction.
- How to use K_p to calculate unknown partial pressures for an equilibrium system.
- How to deduce expressions for K_p for homogeneous and heterogeneous equilibria.
- How changing the temperature will affect the value of the equilibrium constants for endothermic and exothermic reactions.
- That changing the concentration or pressure of reactants or adding a catalyst has no effect on the equilibrium constants.

Exam-style Questions

1 Calculate the partial pressure of hydrogen chloride in the following reaction, given that $p(CH_3OH)$ = 109 kPa, $p(CH_3Cl)$ = 623 kPa, $p(H_2O)$ = 468 kPa and K_p = 52.7.

$$CH_3OH_{(g)} + HCl_{(g)} \rightleftharpoons CH_3Cl_{(g)} + H_2O_{(g)}$$

A 301 kPa

B 55.2 kPa

C 275 kPa

D 50.8 kPa

(1 mark)

2 The following equilibrium establishes at temperature X:

$$CH_{4(g)} + 2H_2O_{(g)} \rightleftharpoons CO_{2(g)} + 4H_{2(g)} \qquad \Delta H = +165 \text{ kJ mol}^{-1}$$

At equilibrium the mixture was found to contain 0.0800 mol dm^{-3} CH_4, 0.320 mol dm^{-3} H_2O, 0.200 mol dm^{-3} CO_2 and 0.280 mol dm^{-3} H_2.

(a) (i) Write an expression for K_c for this equilibrium.

(1 mark)

(ii) Calculate the value of K_c at temperature X, and give its units.

(2 marks)

(b) At a different temperature, Y, the value of K_c was found to be 0.0800 and the equilibrium concentrations were as follows:

Gas	CH_4	H_2O	CO_2	H_2
Concentration (mol dm^{-3})	?	0.560	0.420	0.480

(i) Calculate the equilibrium concentration of CH_4 at this temperature.

(2 marks)

(ii) At another temperature, Z, the value of K_c was found to be 1.20 × 10^{-3}. Suggest whether temperature Z is higher or lower than temperature Y. Explain your answer.

(3 marks)

(c) State how the value of K_c would change if a catalyst was added to the reaction. Explain your answer.

(2 marks)

Module 5 Section 3: Acids, Bases and pH

1. Acids and Bases

Learning Objectives:

- Be able to describe a Brønsted-Lowry acid as a species that donates a proton and a Brønsted-Lowry base as a species that accepts a proton.
- Understand the differences between monobasic, dibasic and tribasic acids.
- Be able to use the term conjugate acid-base pairs.
- Be able to describe the role of H^+ in the reactions of acids with metals and bases (including carbonates, metal oxides and alkalis), using ionic equations.
- Be able to describe how different models developed over time to explain acid–base behaviour.

Specification Reference 5.1.3

There are a few different theories that describe acids and bases. One of those theories is the Brønsted–Lowry theory. Here it is...

Brønsted–Lowry acids and bases

Brønsted–Lowry acids are proton donors — they release hydrogen ions (H^+) when they're mixed with water. For example, for the general acid HA:

$$HA_{(aq)} \rightleftharpoons H^+_{(aq)} + A^-_{(aq)}$$

You never get H^+ ions by themselves in water though — they're always combined with H_2O to form hydroxonium ions, H_3O^+:

$$HA_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)}$$

Brønsted–Lowry bases do the opposite — they're proton acceptors. When they're in solution, they grab hydrogen ions from water molecules. For example, for the general base B:

$$B_{(aq)} + H_2O_{(l)} \rightleftharpoons BH^+_{(aq)} + OH^-_{(aq)}$$

Dissociation in water

Acids and bases dissociate in water. This just means they break up into positively and negatively charged ions. The amount of dissociation depends on how weak or strong the acid or base is. **Strong acids** dissociate (or ionise) almost completely in water — nearly all the H^+ ions will be released. **Strong bases** (like sodium hydroxide) ionise almost completely in water too.

Examples

Hydrochloric acid is a strong acid: $HCl_{(g)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$

Sodium hydroxide is a strong base: $NaOH_{(s)} \rightarrow Na^+_{(aq)} + OH^-_{(aq)}$

These reactions are actually reversible reactions but the equilibrium lies very far to the right, so only the forward reaction is shown in the equation.

Tip: Don't forget — H^+ ions and protons are the same thing.

Weak acids (e.g. ethanoic or citric) dissociate only very slightly in water — so only small numbers of H^+ ions are formed. An equilibrium is set up which lies well over to the left. **Weak bases** (such as ammonia) only slightly dissociate in water too. Just like with weak acids, the equilibrium lies well over to the left.

Examples

Ethanoic acid is a weak acid: $CH_3COOH_{(aq)} + H_2O_{(l)} \rightleftharpoons CH_3COO^-_{(aq)} + H_3O^+_{(aq)}$

Ammonia is a weak base: $NH_{3(aq)} + H_2O_{(l)} \rightleftharpoons NH_4{}^+_{(aq)} + OH^-_{(aq)}$

Tip: Monobasic acids are also known as monoprotic acids, dibasic acids can be called diprotic acids, and tribasic acids can be called triprotic acids.

Monobasic, dibasic and tribasic acids

Acids like HCl and HNO_3 only have one proton per molecule that they can release into solution. These are **monobasic** acids. But some acids, such as sulfuric acid (H_2SO_4) or phosphoric acid (H_3PO_4), have more than one proton per molecule that they can release into solution. Acids that can release two protons into solution are called **dibasic** acids, and acids that can release three protons into solution are **tribasic** acids.

Examples

Sulfuric acid can release two protons, so it's a dibasic acid:

$$H_2SO_{4(aq)} \rightleftharpoons 2H^+_{(aq)} + SO_4{}^{2-}{}_{(aq)}$$

Phosphoric acid can release three protons, so it's a tribasic acid.

$$H_3PO_{4(aq)} \rightleftharpoons 3H^+_{(aq)} + PO_4{}^{3-}{}_{(aq)}$$

Tip: Acids that can release more than one proton into solution are also known by the more general term 'polybasic acids' (or 'polyprotic acids').

Conjugate pairs

Conjugate pairs are species that are linked by the transfer of a proton. They're always on opposite sides of the reaction equation. The species that has lost a proton is the conjugate base and the species that has gained a proton is the conjugate acid. When Brønsted-Lowry acids and bases react together, the equilibrium below is set up:

$$HA + B \rightleftharpoons BH^+ + A^-$$

When HA loses a proton it forms A^- and when A^- gains a proton it forms HA — HA and A^- are linked by proton transfer so are a conjugate pair. HA has gained a proton so is the conjugate acid of A^-. A^- has lost a proton so is the conjugate base of HA.

$$\text{conjugate acid} \rightarrow HA \rightleftharpoons \underset{\substack{\uparrow \\ \text{linked by proton transfer}}}{H^+} + A^- \leftarrow \text{conjugate base}$$

The base, B, takes a proton from the acid, HA, to form BH^+ — so B is the conjugate base of BH^+, and BH^+ is the conjugate acid of B.

$$\text{conjugate base} \rightarrow B + \underset{\substack{\uparrow \\ \text{linked by proton transfer}}}{H^+} \rightleftharpoons BH^+ \leftarrow \text{conjugate acid}$$

So, you get two conjugate pairs when an acid, HA, reacts with a base, B:

conjugate pair 2

$$\underset{\text{acid 1}}{HA} + \underset{\text{base 2}}{B} \rightleftharpoons \underset{\text{acid 2}}{BH^+} + \underset{\text{base 1}}{A^-}$$

conjugate pair 1

Tip: A species is just any type of chemical — it could be an atom, a molecule, an ion...

Conjugate pairs when acids and bases dissolve in water

Water is a special case — it reacts with acids to form a conjugate acid (H_3O^+), and reacts with bases to form a conjugate base (OH^-).

Here's the general equation for the reaction when an acid dissolves in water:

conjugate pair 2

$$\underset{\text{acid 1}}{HA} + \underset{\text{base 2}}{H_2O} \rightleftharpoons \underset{\text{acid 2}}{H_3O^+} + \underset{\text{base 1}}{A^-}$$

conjugate pair 1

Figure 1: A bottle of aqueous sulfuric acid. In this bottle the following equilibrium is established:

$$H_2SO_4 + H_2O \rightleftharpoons H_3O^+ + HSO_4^-$$

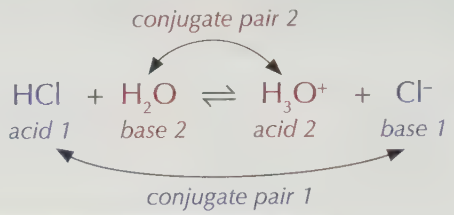
H_2SO_4 and HSO_4^- are a conjugate pair — H_2SO_4 is an acid and HSO_4^- is a base.

Tip: In this reaction, water is acting as a base and is accepting a proton from the acid.

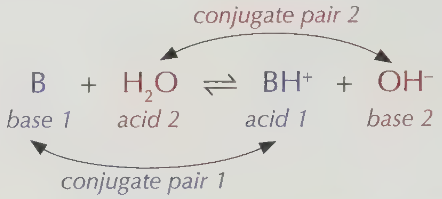
Tip: H_3O^+ is also known as the hydroxonium ion.

Example

Here's the equilibrium for aqueous HCl. Cl^- is the conjugate base of HCl.


conjugate pair 2
$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$
acid 1
base 2
acid 2
base 1
conjugate pair 1

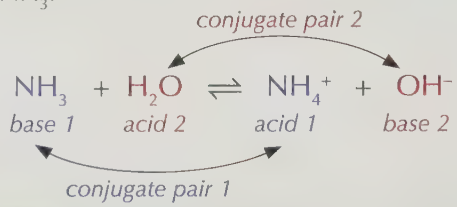
This is the general equation for the reaction when a base dissolves in water:


conjugate pair 2
$B + H_2O \rightleftharpoons BH^+ + OH^-$
base 1
acid 2
acid 1
base 2
conjugate pair 1

Tip: Alkalis like NaOH and KOH produce hydroxide ions (OH^-). The conjugate acid of hydroxide ions is water.

Example

Here's the equilibrium when NH_3 is dissolved in water. NH_4^+ is the conjugate acid of NH_3.


conjugate pair 2
$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$
base 1
acid 2
acid 1
base 2
conjugate pair 1

Identifying conjugate pairs

In your exams, you need to be able to identify the conjugate pairs formed in a reaction. It's easy enough to do — just find the species that are linked by proton transfer and work out which one is the acid and which one is the base.

Tip: Two species can't be a conjugate pair if they are on the same side of the equation — they have to be on opposite sides.

Example

When ammonium nitrate, NH_4NO_3 is dissolved in water the following equilibrium is set up: $NH_4^+ + NO_3^- \rightleftharpoons HNO_3 + NH_3$

Identify the conjugate pairs in this reaction.

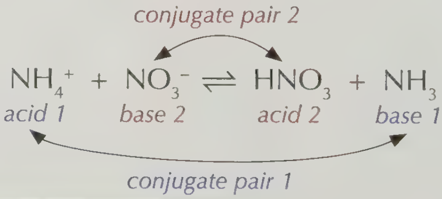
NH_4^+ and NH_3 are linked by proton transfer so they must form one conjugate pair.

NO_3^- and HNO_3 are also linked by proton transfer so they must be the other conjugate pair.

In the NH_4^+/NH_3 conjugate pair, NH_4^+ donates a proton so must be the conjugate acid — NH_3 accepts a proton so must be the conjugate base.

In the NO_3^-/HNO_3 pair, NO_3^- accepts a proton so must be the conjugate base — HNO_3 donates a proton so must be the conjugate acid.

So the conjugate pairs in this reaction are:


conjugate pair 2
$NH_4^+ + NO_3^- \rightleftharpoons HNO_3 + NH_3$
acid 1
base 2
acid 2
base 1
conjugate pair 1

Reactions of acids

There are a few reactions of acids that you need to know about.

Reactions with metals

Reactive metals react with acids forming a salt and releasing hydrogen gas. The metal atoms donate electrons to the H^+ ions in the acid solution. The metal atoms are oxidised and the H^+ ions are reduced.

Example

Magnesium reacts with hydrochloric acid to produce magnesium chloride and hydrogen:

Full equation: $Mg_{(s)} + 2HCl_{(aq)} \rightarrow MgCl_{2(aq)} + H_{2(g)}$

Ionic equation: $Mg_{(s)} + 2H^+_{(aq)} \rightarrow Mg^{2+}_{(aq)} + H_{2(g)}$

Oxidation states: 0 +1 +2 0

Oxidation *Reduction*

Tip: Don't forget — oxidation is the loss of electrons, reduction is the gain of electrons.

Reactions with carbonates

Carbonates react with acids to produce carbon dioxide, water and a salt.

Example

Sodium carbonate reacts with sulfuric acid to produce carbon dioxide, water and sodium sulfate:

Full equation: $Na_2CO_{3(s)} + H_2SO_{4(aq)} \rightarrow Na_2SO_{4(aq)} + CO_{2(g)} + H_2O_{(l)}$

Ionic equation: $CO_3^{2-}{}_{(aq)} + 2H^+_{(aq)} \rightarrow H_2O_{(l)} + CO_{2(g)}$

Figure 2: Sodium carbonate reacting with acid. The bubbles are the CO_2 gas that's being given off.

Reactions with bases and alkalis

Acids produce H^+ ions when dissolved in water and alkalis produce OH^- ions. Acids and alkalis neutralise each other to form water. The other ions present form a salt. The ionic equation for the reaction of an acid with an alkali is:

$$H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)}$$

Example

Hydrochloric acid reacts with potassium hydroxide to produce potassium chloride and water:

Full equation: $HCl_{(aq)} + KOH_{(aq)} \rightarrow KCl_{(aq)} + H_2O_{(l)}$

Ionic equation: $H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)}$

Tip: Alkalis are bases that release hydroxide ions (OH^-) when they dissolve in water.

Acids can react with insoluble bases in a similar way. Here's how an acid neutralises an insoluble base:

$$2H^+_{(aq)} + O^{2-}_{(s)} \rightarrow H_2O_{(l)}$$

Tip: Lots of metal oxides are insoluble bases.

Example

Hydrochloric acid reacts with solid copper oxide to produce copper chloride and water:

Full equation: $2HCl_{(aq)} + CuO_{(s)} \rightarrow CuCl_{2(aq)} + H_2O_{(l)}$

Ionic equation: $2H^+_{(aq)} + CuO_{(s)} \rightarrow H_2O_{(l)} + Cu^{2+}_{(aq)}$

Exam Tip

Make sure you can write full and ionic equations for the reactions of acids with metals, carbonates, bases and alkalis — you could be asked about any of these in your exams.

Development of acid-base theory

HOW SCIENCE WORKS

Scientific theories can take years to develop. A scientist will come up with an idea, and then someone else will find holes in the theory and make changes to improve it. This is how the Brønsted-Lowry theory of acids and bases came about.

Lavoisier came up with the first theory of acids and bases in the 18th century. He didn't know the formulas of compounds like hydrochloric acid but he did know that sulfuric acid had the formula H_2SO_4 and nitric acid had the formula HNO_3. So he proposed that acids had to have oxygen in them. It was later shown that acids like hydrochloric acid (HCl) and hydrogen sulfide (H_2S) don't have any oxygen in them at all.

At the end of the 19th century, a chemist called Arrhenius suggested that acids release protons in aqueous solution, whilst bases release hydroxide ions. He said that when acids and bases react together they form water and a salt. This is true for loads of examples, but doesn't work for bases such as ammonia (NH_3), which don't contain any hydroxide ions.

Figure 3: *J.N. Brønsted — co-author of the Brønsted–Lowry theory.*

Brønsted and Lowry came up with their definition of acids and bases independently of one another. It's clearly based on Arrhenius' theory, but broadens the definition of a base to be a proton acceptor. They also came up with the idea that acids and bases react to form conjugate pairs, rather than a salt and water. This definition currently explains most of our observations, so is one of the theories we still use today — around 100 years later.

Practice Questions — Application

Q1 Write full and ionic equations for the reaction of:
- a) hydrochloric acid (HCl) with sodium metal (Na).
- b) sulfuric acid (H_2SO_4) with solid calcium carbonate ($CaCO_3$).
- c) nitric acid (HNO_3) with potassium hydroxide solution (KOH).
- d) hydrocyanic acid (HCN) with solid sodium oxide (Na_2O).

Q2 Identify the conjugate acid-base pairs in the following reactions by labelling them 'acid 1' and 'base 1' and 'acid 2' and 'base 2':
- a) $H_2CO_{3(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + HCO_3^-{}_{(aq)}$
- b) $CH_3NH_{2(aq)} + H_2O_{(l)} \rightleftharpoons CH_3NH_3^+{}_{(aq)} + OH^-_{(aq)}$
- c) $CH_3COO^-_{(aq)} + NH_4^+{}_{(aq)} \rightleftharpoons CH_3COOH_{(aq)} + NH_{3(aq)}$
- d) $HCl_{(aq)} + OH^-_{(aq)} \rightleftharpoons Cl^-_{(aq)} + H_2O_{(l)}$

Practice Questions — Fact Recall

Q1 What is the definition of:
- a) a Brønsted-Lowry acid?
- b) a Brønsted-Lowry base?

Q2 Give both the definition and an example of the following substances:
- a) a monobasic acid
- b) a dibasic acid
- c) a tribasic acid

Q3 a) What type of acid dissociates almost completely in water?
- b) What type of base dissociates only slightly in water?

Q4 What is a conjugate pair?

Q5 What products are formed when an acid reacts with:
- a) a metal?
- b) a carbonate?
- c) a base?

2. pH Calculations

There are lots of pH calculations that you need to know how to do for your exams. The next few pages tell you everything you need to know to get started.

The pH scale

pH is a measure of the hydrogen ion concentration in a solution. The concentration of hydrogen ions in a solution can vary enormously, so those wise chemists of old decided to express the concentration on a logarithmic scale, called the pH scale. pH can be calculated using the following equation:

$$\text{pH} = -\log_{10}[\text{H}^+]$$

$[\text{H}^+]$ is the concentration of hydrogen ions in a solution, measured in mol dm^{-3}. So, if you know the hydrogen ion concentration of a solution, you can calculate its pH by sticking the numbers into the formula.

Example — Maths Skills

A solution of hydrochloric acid has a hydrogen ion concentration of 0.010 mol dm^{-3}. What is the pH of the solution?

$$\text{pH} = -\log_{10}[\text{H}^+]$$
$$= -\log_{10}[0.010] = \mathbf{2.00}$$

Just substitute the [H$^+$] value into the pH formula and solve.

The pH scale normally goes from 0 (very acidic) to 14 (very alkaline). pH 7 is regarded as being neutral. Solutions that have a very low pH include strong acids such as HCl and H_2SO_4. Strong bases such as NaOH and KOH have a very high pH. Pure water has a pH of 7 and is neutral.

Calculating [H⁺] from pH

If you've got the pH of a solution, and you want to know its hydrogen ion concentration, then you need the inverse of the pH formula:

$$[\text{H}^+] = 10^{-\text{pH}}$$

Now you can use this formula to find $[\text{H}^+]$.

Example — Maths Skills

A solution of nitric acid has a pH of 1.52.
What is the hydrogen ion concentration of this solution?

$$[\text{H}^+] = 10^{-\text{pH}}$$
$$= 10^{-1.52}$$
$$= 0.030 \text{ mol dm}^{-3}$$
$$= \mathbf{3.0 \times 10^{-2} \text{ mol dm}^{-3}}$$

Just substitute the pH value into the inverse pH formula and solve.

Practice Questions — Application

Q1 A solution of hydrochloric acid (HCl) has a hydrogen ion concentration of 0.05 mol dm^{-3}. Calculate the pH of this solution.

Q2 A solution of nitric acid (HNO_3) has a pH of 2.86. Calculate the concentration of hydrogen ions in this solution.

Q3 Calculate the pH of a solution of hydrochloric acid (HCl) with a hydrogen ion concentration of 0.02 mol dm^{-3}.

Learning Objectives:

- Be able to use the expressions $\text{pH} = -\log[\text{H}^+]$ and $[\text{H}^+] = 10^{-\text{pH}}$
- Be able to calculate pH and related quantities for strong, monobasic acids.

Specification Reference 5.1.3

Tip: To calculate logarithms you need to use the 'log' button on your calculator. Different calculators work differently so make sure you know how to calculate logs on yours.

Exam Tip
In the exam, always give your calculated pH values to the same number of decimal places as there are significant figures in your original value. If you're unsure, give your answer to 2 d.p.

Figure 1: pH can be measured using a pH meter like this one (see page 356).

Exam Tip
If your calculation involves a power, like 10^x, your answer should be to the same number of significant figures as the number of decimal places in x. This is a bit different to the normal significant figures rules.

pH of strong, monobasic acids

Monobasic means that each molecule of an acid will release one proton when it dissociates. Hydrochloric acid (HCl) and nitric acid (HNO_3) are strong acids so they ionise fully:

$$HCl_{(aq)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$$

HCl and HNO_3 are also monobasic, so each mole of acid produces one mole of hydrogen ions. This means the H^+ concentration is the same as the acid concentration. So, if you know the concentration of the acid you know the H^+ concentration and you can calculate the pH.

Tip: The strength of an acid has nothing to do with its concentration. How strong an acid is depends on how much it dissociates in water. The concentration is just how diluted the acid is.

Tip: Monobasic acids are also known as monoprotic acids — meaning they release one proton.

Exam Tip
Acids like H_2SO_4 are dibasic — they release two protons when they dissociate. Don't worry though, you won't have to do pH calculations for dibasic acids in the exam.

Examples — **Maths Skills**

Calculate the pH of 0.10 mol dm^{-3} hydrochloric acid:

$[HCl] = [H^+] = 0.10$ mol dm^{-3}. So:

$$\begin{aligned} pH &= -\log_{10} [H^+] \\ &= -\log_{10} 0.10 \\ &= 1.00 \end{aligned}$$

Calculate the pH of 0.050 mol dm^{-3} nitric acid:

$[HNO_3] = [H^+] = 0.050$ mol dm^{-3}. So:

$$\begin{aligned} pH &= -\log_{10} 0.050 \\ &= 1.30 \end{aligned}$$

If a solution of hydrochloric acid has a pH of 2.45, what is the concentration of the acid?

$[HCl] = [H^+] = 10^{-pH}$. So:

$$\begin{aligned} [HCl] &= 10^{-2.45} \\ &= 3.5 \times 10^{-3} \text{ mol dm}^{-3} \end{aligned}$$

Hydrochloric acid, 6 M
HCl 6M

Figure 2: Hydrochloric acid is a strong acid.

Practice Questions — Application

Q1 Hydrochloric acid (HCl) is a strong monobasic acid. Calculate the pH of a 0.08 mol dm^{-3} solution of HCl.

Q2 Nitric acid (HNO_3) is a strong monobasic acid. Calculate the pH of a 0.12 mol dm^{-3} solution of HNO_3.

Q3 A solution of hydrochloric acid has a pH of 0.96. Calculate the concentration of this hydrochloric acid solution.

Q4 A solution of nitric acid has a pH of 1.28. Calculate the concentration of this nitric acid solution.

Practice Questions — Fact Recall

Q1 Write out the expression that defines pH.

Q2 Write out the equation that you would need to calculate the hydrogen ion concentration of an acid, given its pH.

Q3 Explain what is meant by the term monobasic.

Q4 What is the relationship between the concentration of H^+ ions and the acid concentration in strong monobasic acids?

Exam Tip
Calculating the pH of acids from their concentrations comes up in loads of calculations so you need to be really confident that you know how to do it.

3. The Ionic Product of Water

The ionic product of water (also known as K_w) is really just another equilibrium constant. "So why do I need to know about it?", I hear you cry. Well, mainly because it comes in handy for calculating the pH of strong bases. Read on...

Learning Objectives:

- Be able to state and use the expression for the ionic product of water, K_w.
- Be able to describe the constancy of K_w with changes in concentration.
- Be able to describe the qualitative effect on K_w of changing temperature for exothermic and endothermic reactions.
- Be able to explain how K_w controls the position of equilibrium on changing concentration and temperature.
- Be able to calculate pH and related quantities for strong bases, using K_w.

Specification Reference
5.1.2, 5.1.3

What is K_w?

Water dissociates into hydroxonium ions and hydroxide ions. So this equilibrium exists in water:

$$H_2O_{(l)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}$$

If you remove an H_2O from both sides, this simplifies to:

$$H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$$

And, just like for any other equilibrium reaction, you can apply the equilibrium law and write an expression for the equilibrium constant:

$$K_c = \frac{[H^+][OH^-]}{[H_2O]}$$

Water only dissociates a tiny amount, so the equilibrium lies well over to the left. There's so much water compared to the amounts of H^+ and OH^- ions that the concentration of water is considered to have a constant value. So if you multiply the expression you wrote for K_c (which is a constant) by $[H_2O]$ (another constant), you get a constant. This new constant is called the **ionic product of water** and it is given the symbol K_w.

$$K_w = K_c \times [H_2O] = \frac{[H^+][OH^-]}{\cancel{[H_2O]}} \times \cancel{[H_2O]}$$

So... $\boxed{K_w = [H^+][OH^-]}$

K_w always has the same value for an aqueous solution at a given temperature. For example, at 298 K (25 °C), K_w has a value of 1.00×10^{-14} mol^2 dm^{-6}.

Tip: See page 321 for more on the equilibrium constant, K_c.

K_w behaves like other equilibrium constants:

- The value of K_w is fixed at a given temperature. So if the concentration of one thing in the equilibrium mixture changes then the concentrations of the others must change to keep the value of K_w the same.
- Changing the temperature of the solution changes the value of K_w — dissociation of water is an endothermic process, so warming the solution shifts the equilibrium to the right (it dissociates more), and the value of K_w increases. Cooling the solution shifts the equilibrium to the left (there is less dissociation), and the value of K_w decreases.

Tip: The units of K_w are always mol^2 dm^{-6} because mol dm^{-3} × mol dm^{-3} = mol^2 dm^{-6}.

Finding the pH of water

The pH of water is not always exactly 7 — it actually varies depending on the temperature. You can calculate the pH of water using K_w. The expression for K_w is $K_w = [H^+][OH^-]$. But in pure water, there is always one H^+ ion for each OH^- ion. So $[H^+] = [OH^-]$. That means if you are dealing with pure water, you can say that:

$$K_w = [H^+]^2$$

If you want to find the pH of water at a particular temperature, substitute the value for K_w at that temperature into the equation above, solve it to find $[H^+]$ by taking the square root of both sides, then use $pH = -\log_{10}[H^+]$ to find the pH.

Exam Tip
Remember — K_w only equals $[H^+]^2$ in pure water. If you're asked to write an expression for K_w, always give $K_w = [H^+][OH^-]$.

Tip: Although the pH of water changes with temperature, water is always described as neutral (not acidic or alkaline) because $[H^+]$ always equals $[OH^-]$.

Example **Maths Skills**

At 50 °C, the value of K_w is 5.48×10^{-14} mol² dm⁻⁶.
Calculate the pH of pure water at this temperature.

- Substituting in K_w gives $5.48 \times 10^{-14} = [H^+]^2$
- So $[H^+] = \sqrt{5.48 \times 10^{-14}} = 2.34... \times 10^{-7}$
- $\text{pH} = -\log_{10} [H^+] = -\log_{10} (2.34... \times 10^{-7}) = 6.631$

So the pH of pure water at 50 °C is **6.631**.

Practice Questions — Application

Q1 Calculate the pH of pure water at 30 °C.
The value of K_w at 30 °C is 1.47×10^{-14} mol² dm⁻⁶.

Q2 Calculate the pH of pure water at 40 °C.
The value of K_w at 40 °C is 2.92×10^{-14} mol² dm⁻⁶.

Figure 1: Sodium hydroxide turns this Universal indicator paper dark blue, which shows that it has a high pH.

Finding the pH of strong bases

Sodium hydroxide (NaOH) and potassium hydroxide (KOH) are strong bases that fully ionise in water — they donate one mole of OH^- ions per mole of base. This means that the concentration of OH^- ions is the same as the concentration of the base. So for 0.02 mol dm⁻³ sodium hydroxide solution, $[OH^-]$ is also 0.02 mol dm⁻³. But to work out the pH you need to know $[H^+]$ — luckily this is linked to $[OH^-]$ through the ionic product of water, K_w:

$$K_w = [H^+][OH^-]$$

If you know $[OH^-]$ for a strong aqueous base and K_w at a certain temperature, you can work out $[H^+]$ and then the pH. Just follow these steps:

Step 1: Find the values of K_w and $[OH^-]$. You may be told these in the question or you may have to work them out.

Step 2: Rearrange the equation, substitute the values for K_w and $[OH^-]$ into the equation, and solve it to find $[H^+]$.

Step 3: Once you know $[H^+]$, substitute this into the pH equation ($\text{pH} = -\log_{10}[H^+]$) and solve it to find out the pH.

Tip: It doesn't matter whether water is pure or part of a solution — K_w is always the same at the same temperature.

Exam Tip
Don't worry — you don't have to memorise any values of K_w. You'll always be told K_w in the question if you need to use it.

Example **Maths Skills**

The value of K_w at 298 K is 1.0×10^{-14} mol² dm⁻⁶.

Find the pH of 0.100 mol dm⁻³ NaOH at 298 K.

1. Find the values of K_w and $[OH^-]$:
    - The value of K_w is given in the question as 1.0×10^{-14} mol² dm⁻⁶
    - NaOH is a strong base so will donate one mole of OH^- ions per mole of base. The concentration of NaOH is 0.100 mol dm⁻³ so $[OH^-]$ must be 0.100 mol dm⁻³.
2. Substitute the values of K_w and $[OH^-]$ into the K_w equation:

$$K_w = [H^+][OH^-] \text{ so } [H^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{0.100} = 1.0 \times 10^{-13} \text{ mol dm}^{-3}$$

3. Substitute the value of $[H^+]$ into the pH equation:

$$\text{pH} = -\log_{10}(1.0 \times 10^{-13}) = \mathbf{13.00}$$

Practice Questions — Application

Q1 Calculate the pH of a 0.200 mol dm^{-3} solution of KOH at 50 °C. The value of K_w at 50 °C is 5.48×10^{-14} $mol^2\ dm^{-6}$.

Q2 Calculate the pH of a 0.155 mol dm^{-3} solution of NaOH at 20 °C. The value of K_w at 20 °C is 6.81×10^{-15} $mol^2\ dm^{-6}$.

Q3 Calculate the pH of a 0.0840 mol dm^{-3} solution of KOH at 10 °C. The value of K_w at 10 °C is 2.93×10^{-15} $mol^2\ dm^{-6}$.

Finding the concentration of strong bases

If you know the pH of a strong base you can use K_w to find its concentration. Here's what you have to do:

Step 1: Use the equation $[H^+] = 10^{-pH}$ to find the value of $[H^+]$ in the solution.

Step 2: Substitute your value for $[H^+]$ along with the value of K_w into the K_w equation and solve it to find $[OH^-]$.

Step 3: Because strong bases fully dissociate, $[OH^-]$ is the same as the concentration of the base.

Example — Maths Skills

A solution of NaOH has a pH of 12.50 at 30 °C. The value of K_w at 30 °C is 1.47×10^{-14} $mol^2\ dm^{-6}$. Calculate the concentration of this NaOH solution.

1. Find $[H^+]$:

$$[H^+] = 10^{-pH} = 10^{-12.50} = 3.16... \times 10^{-13}$$

2. Substitute $[H^+]$ and the value for K_w into the K_w equation:

$$K_w = [H^+][OH^-] \text{ so } [OH^-] = \frac{K_w}{[H^+]} = \frac{1.47 \times 10^{-14}}{3.16... \times 10^{-13}} = 0.046 \text{ mol dm}^{-3}$$

3. Because NaOH is a strong base [NaOH] = $[OH^-]$ so the concentration of the NaOH solution is **0.046 mol dm^{-3}**.

Tip: This is very similar to finding the pH of strong bases — you just have to do the steps in reverse.

Exam Tip
Make sure you know how to find the pH and the concentration of a strong base — you could be asked to do either in the exams.

Tip: The temperature at which measurements are taken and the temperature of K_w have to match — otherwise the calculation won't be valid.

Practice Questions — Application

Q4 Find the concentration of a solution of KOH that has a pH of 12.40 at 20 °C. The value of K_w at 20 °C is 6.8×10^{-15} $mol^2\ dm^{-6}$.

Q5 Find the concentration of a solution of NaOH that has a pH of 13.98 at 40 °C. The value of K_w at 40 °C is 2.92×10^{-14} $mol^2\ dm^{-6}$.

Q6 Find the concentration of a solution of KOH that has a pH of 13.25 at 30 °C. The value of K_w at 30 °C is 1.47×10^{-14} $mol^2\ dm^{-6}$.

Practice Questions — Fact Recall

Q1 Write an expression for K_w.

Q2 What are the units of K_w?

Q3 Explain why $K_w = [H^+]^2$ for pure water.

4. The Acid Dissociation Constant

You've already seen how to calculate the pH of strong acids and strong bases. Now get ready for part three: calculating the pH of weak acids.

Learning Objectives:

- Be able to define and use the acid dissociation constant, K_a, for the extent of acid dissociation.
- Understand the limitations of using approximations to K_a related calculations for 'stronger' weak acids.
- Be able to describe the constancy of K_a with changes in concentration.
- Be able to describe the qualitative effect on K_a of changing temperature for exothermic and endothermic reactions.
- Be able to explain how K_a controls the position of equilibrium on changing concentration and temperature.
- Be able to carry out calculations of pH, K_a or related quantities, for a weak monobasic acid using approximations.
- Understand the relationship between K_a and pK_a.

Specification Reference
5.1.2, 5.1.3

What is the acid dissociation constant?

Weak acids don't ionise fully in solution, so the $[H^+]$ isn't the same as the acid concentration. This makes it a bit trickier to find their pH. You have to use yet another equilibrium constant — the **acid dissociation constant**, K_a. The units of K_a are mol dm^{-3} and the equation for K_a is derived as follows:

For a weak monobasic aqueous acid, HA, you get the equilibrium:

$$HA_{(aq)} \rightleftharpoons H^+_{(aq)} + A^-_{(aq)}$$

As only a tiny amount of HA dissociates, you can assume that [HA] at the start of the reaction is the same as [HA] at equilibrium, i.e.

$$[HA] \gg [H^+], \text{ so } [HA]_{(start)} \approx [HA]_{(equilibrium)}$$

So if you apply the equilibrium law, you get:

$$K_a = \frac{[H^+]\,[A^-]}{[HA]_{start}}$$

When dealing with weak acids, you can assume that dissociation of the acid is much greater than dissociation of water. This means you can assume that all the H^+ ions come from the acid, so for a monobasic acid, $[H^+] \approx [A^-]$.

So the formula for K_a can be simplified to: $K_a = \dfrac{[H^+]^2}{[HA]}$

In order to use the expression for K_a properly, you need to know the limitations under which it works. The assumptions made to find K_a only work for **weak acids**. Stronger acids **dissociate more** in solution, so the difference between $[HA]_{start}$ and $[HA]_{equilibrium}$ becomes significant, and the assumption that $[HA]_{start} \approx [HA]_{equilibrium}$ is no longer valid.

HOW SCIENCE WORKS

K_a behaves like other equilibrium constants:

- The value of K_a is fixed at a given temperature. So if the concentration of one thing in the equilibrium mixture changes then the concentrations of the others must change to keep the value of K_a the same.
- Changing the temperature of the solution changes the value of K_a.
  If dissociation is endothermic, warming the solution shifts the equilibrium to the right (it dissociates more), so K_a increases, and vice versa.
  If dissociation is exothermic, warming the solution shifts the equilibrium to the left, so K_a decreases, and vice versa.

Calculations using K_a

You can rearrange the expression of K_a in order to find the concentration of a weak acid, and hence its pH. You can also use the pH and concentration of a weak acid to find K_a for that acid at a particular temperature.

Tip: K_a is a type of equilibrium constant, so the formula for K_a is based on the one for K_c. It applies to a particular acid at a specific temperature, regardless of the concentration.

Finding the pH of weak acids

You can use K_a to find the pH of a weak acid. Just follow these steps.

Step 1: Write an expression for K_a for the weak acid. (You can write out the equilibrium equation first if it helps you write this expression.)

Step 2: Rearrange the equation and substitute in the values for K_a and [HA] to find $[H^+]^2$.

Step 3: Take the square root of the number to find $[H^+]$.

Step 4: Substitute $[H^+]$ into the pH equation to find the pH.

Example **Maths Skills**

Find the pH of a 0.020 mol dm^{-3} solution of propanoic acid (CH_3CH_2COOH) at 298 K. K_a for propanoic acid at this temperature is 1.30×10^{-5} mol dm^{-3}.

1. First write an expression for K_a for the weak acid.
   Propanoic acid equilibrium: $CH_3CH_2COOH \rightleftharpoons H^+ + CH_3CH_2COO^-$

$$\text{So, } K_a = \frac{[H^+][CH_3CH_2COO^-]}{[CH_3CH_2COOH]} = \frac{[H^+]^2}{[CH_3CH_2COOH]}$$

2. Rearrange the equation to find $[H^+]^2$:

$$[H^+]^2 = K_a[CH_3CH_2COOH]$$
$$= (1.30 \times 10^{-5}) \times 0.020 = 2.60 \times 10^{-7}$$

3. Take the square root of this number to find $[H^+]$:

$$[H^+] = \sqrt{2.60 \times 10^{-7}}$$
$$= 5.09... \times 10^{-4} \text{ mol dm}^{-3}$$

4. Use $[H^+]$ to find the pH of the acid:

$$pH = -\log_{10} [H^+]$$
$$= -\log_{10} 5.09... \times 10^{-4} = \mathbf{3.29}$$

Figure 1: Lemon juice contains citric acid. It turns this universal indicator paper orange, which shows that it's a weak acid.

Finding the concentration of weak acids

If you already know the pH you can use K_a to find the concentration of the acid. You don't need to know anything new for this type of calculation — you use the same formulas you used to find the pH.

Step 1: Substitute the pH into the inverse pH equation to calculate $[H^+]$.

Step 2: Write an expression for K_a.

Step 3: Rearrange the equation to give the concentration of the acid.

Step 4: Substitute the values for K_a and $[H^+]$ into the equation and solve it.

Exam Tip
It's really important to show all the steps of your working in exam questions — that way the examiner can give you some marks for your method even if your final answer is wrong.

Example **Maths Skills**

The pH of an ethanoic acid (CH_3COOH) solution is 3.02 at 298 K. Calculate the molar concentration of this solution. The K_a of ethanoic acid is 1.75×10^{-5} mol dm^{-3} at 298 K.

1. Use the pH of the acid to find $[H^+]$:

$$[H^+] = 10^{-pH}$$
$$= 10^{-3.02}$$
$$= 9.5... \times 10^{-4} \text{ mol dm}^{-3}$$

2. Write an expression for K_a:

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = \frac{[H^+]^2}{[CH_3COOH]}$$

3. Rearrange it to give $[CH_3COOH]$:

$$[CH_3COOH] = \frac{[H^+]^2}{K_a}$$

4. Substitute in K_a and $[H^+]$ and solve the equation to find $[CH_3COOH]$:

$$[CH_3COOH] = \frac{(9.5... \times 10^{-4})^2}{1.75 \times 10^{-5}} = \mathbf{0.052 \text{ mol dm}^{-3}}$$

Tip: Remember, you can write out the equilibrium equation to help with Step 2 if you like.

Exam Tip
If you can't work out the chemical formula of an acid, just use HA instead and you might still get the marks.

Exam Tip
You need to be able to do all three types of calculation in the exams — any one of them could crop up so make sure you understand these examples.

Finding the K_a of weak acids

If you know both the concentration and the pH, you can use them to find the K_a of the weak acid. Just find $[H^+]$ (as shown in the previous example), substitute the values you know into the expression for K_a and solve.

Example — Maths Skills

A solution of 0.162 mol dm^{-3} HCN has a pH of 5.05 at 298 K. What is the value of K_a for HCN at 298 K?

1. Use the pH of the acid to find $[H^+]$:

$$\begin{aligned}[H^+] &= 10^{-pH}\\ &= 10^{-5.05}\\ &= 8.9... \times 10^{-6}\ \text{mol dm}^{-3}\end{aligned}$$

2. Write an expression for K_a:

$$K_a = \frac{[H^+][CN^-]}{[HCN]} = \frac{[H^+]^2}{[HCN]}$$

3. Substitute in the values for $[H^+]$ and $[HCN]$:

$$K_a = \frac{[H^+]^2}{[HCN]} = \frac{(8.9... \times 10^{-6})^2}{0.162} = \mathbf{4.9 \times 10^{-10}\ mol\ dm^{-3}}$$

The logarithmic constant, pK_a

The value of K_a varies massively from one acid to the next. This can sometimes make the numbers difficult to manage so to make life easier, scientists often use the pK_a instead. pK_a is calculated from K_a in exactly the same way as pH is calculated from $[H^+]$ — and vice versa:

$$\text{p}K_a = -\log_{10}(K_a) \qquad K_a = 10^{-\text{p}Ka}$$

So if an acid has a K_a value of 1.5×10^{-7} mol dm^{-3}, then:

$$\begin{aligned}\text{p}K_a &= -\log_{10}(K_a)\\ &= -\log_{10}(1.5 \times 10^{-7})\\ &= 6.82\end{aligned}$$

Tip: Notice how pK_a values aren't annoyingly tiny like K_a values.

And if an acid has a pK_a value of 4.32, then:

$$\begin{aligned}K_a &= 10^{-\text{p}Ka}\\ &= 10^{-4.32}\\ &= 4.8 \times 10^{-5}\ \text{mol dm}^{-3}\end{aligned}$$

Tip: The larger the pK_a, the weaker the acid. Strong acids have very small pK_a values.

Just to make things that bit more complicated, there might be a pK_a value in a 'find the pH' type of question. If so, you need to convert it to K_a so that you can use the K_a expression.

Example — Maths Skills

Calculate the pH of 0.050 mol dm^{-3} methanoic acid (HCOOH). Methanoic acid has a pK_a of 3.75 at 298 K.

1. Convert the pK_a value to a K_a value:

$$\begin{aligned}K_a &= 10^{-\text{p}Ka}\\ &= 10^{-3.75}\\ &= 1.7... \times 10^{-4}\ \text{mol dm}^{-3}\end{aligned}$$

Tip: These are the same steps as you followed on page 346 but with an extra step (converting the pK_a into K_a) at the beginning.

2. Write out an expression for K_a:

$$K_a = \frac{[H^+][HCOO^-]}{[HCOOH]} = \frac{[H^+]^2}{[HCOOH]}$$

3. Rearrange it to give $[H^+]^2$:

$$[H^+]^2 = K_a[HCOOH]$$
$$= 1.7... \times 10^{-4} \times 0.050$$
$$= 8.8... \times 10^{-6}$$

4. Take the square root to get $[H^+]$:

$$[H^+] = \sqrt{8.8... \times 10^{-6}}$$
$$= 2.9... \times 10^{-3} \text{ mol dm}^{-3}$$

5. Substitute $[H^+]$ into the pH equation and solve:

$$\text{pH} = -\log (2.9... \times 10^{-3}) = \mathbf{2.53}$$

Exam Tip
pH values for weak acids are usually between 2 and 5. If you get an answer much bigger or smaller than this in your exam, double-check your calculation — you may have gone wrong somewhere.

It works the other way round too. Sometimes you are asked to calculate K_a but have to give your answer as a pK_a value. In this case, you just work out the K_a value as usual and then convert it to pK_a — and Bob's your pet hamster.

Practice Questions — Application

Q1 A solution of the weak acid, hydrocyanic acid (HCN) has a concentration of 2.0 mol dm^{-3}. The K_a of this acid at 25 °C is 4.9×10^{-10} mol dm^{-3}.
  a) Write down an expression for the K_a of this acid.
  b) Calculate the pH of this solution at 25 °C.

Q2 A sample of the weak acid nitrous acid (HNO_2) has a pH of 3.80 in solution at 25 °C. The K_a of this acid at 25 °C is 4.0×10^{-4} mol dm^{-3}. Determine the concentration of this solution at 25 °C.

Q3 A 0.280 mol dm^{-3} solution of a weak acid (HA) has a pH of 4.11 at 25 °C. Calculate the K_a of this acid at 25 °C.

Q4 Methanoic acid (HCOOH) has a K_a of 1.8×10^{-4} mol dm^{-3} at 298 K. The pH of a solution of methanoic acid was measured to be 3.67 at 298 K. Determine the concentration of this solution of HCOOH.

Q5 Ethanoic acid has a pK_a of 4.78 at 298 K. Determine the K_a of ethanoic acid at 298 K.

Q6 A 0.154 mol dm^{-3} weak acid solution has a pH of 4.50 at 45 °C. Calculate the pK_a of this acid at 45 °C.

Q7 The pK_a of hydrofluoric acid (HF) is 3.14 at a certain temperature. Calculate the concentration of a solution of hydrofluoric acid that has a pH of 3.20 at this temperature.

Q8 A weak acid (HX) has a pK_a of 4.50 at 25 °C. Calculate the pH of a 0.60 mol dm^{-3} solution of this acid at 25 °C.

Exam Tip
You'll almost certainly have to use expressions for terms like pH and pK_a in the exam so you really, really need to make sure that you know the formulas. Have a look at page 545 for a summary of all the formulas in this section.

Practice Questions — Fact Recall

Q1 What are the units for K_a?

Q2 a) Write an expression for the K_a of a general weak acid (HA).
  b) Rearrange this equation to give an expression for calculating [HA].

Q3 a) Write out the expression that defines pK_a.
  b) Rearrange this equation to give an expression for K_a.

Learning Objectives:

- Be able to describe a buffer solution as a system that minimises pH changes on addition of small amounts of an acid or a base.
- Be able to describe the formation of a buffer solution from a weak acid and a salt of the weak acid, e.g. CH_3COOH/CH_3COONa, or from an excess of a weak acid and a strong alkali, e.g. excess CH_3COOH/NaOH
- Be able to explain the role of the conjugate acid-base pair in an acid buffer solution, e.g. CH_3COOH/CH_3COO^-, in the control of pH.
- Be able to explain the control of blood pH by the carbonic acid–hydrogencarbonate buffer system.

Specification Reference 5.1.3

Tip: The acid has to be a weak acid — you can't make an acidic buffer with a strong acid.

5. Buffer Action

Sometimes, it's useful to have a solution that doesn't change pH when small amounts of acid or base are added to it. That's where buffers come in handy.

What is a buffer?

A **buffer** is a solution that minimises changes in pH when small amounts of acid or base are added. A buffer doesn't stop the pH from changing completely — it does make the changes very slight though. Buffers only work when you add small amounts of acid or base — put too much in and they won't be able to cope. You get acidic buffers and basic buffers — but you only need to know about acidic ones.

Acidic buffers

Acidic buffers have a pH of less than 7 — they're made by setting up an equilibrium between a weak acid and its conjugate base. They can resist a change in pH when either an acid or a base is added to the solution. There are two ways of preparing acidic buffers that you need to know about.

1. Making a buffer from a weak acid and the salt of its conjugate base

If you mix a weak acid with a salt of its conjugate base, then a small amount of the acid will dissociate, but some will remain undissociated. The salt will fully dissociate to form the conjugate base of the acid in the solution. So the solution will contain a mixture of a weak acid and its conjugate base, and can act as an acidic buffer.

Example

A mixture of ethanoic acid (CH_3COOH) and sodium ethanoate ($CH_3COO^-Na^+$) is an **acidic buffer**. Ethanoic acid is a weak acid, so it only slightly dissociates:

$$CH_3COOH_{(aq)} \rightleftharpoons H^+_{(aq)} + CH_3COO^-_{(aq)}$$

But the salt fully dissociates into its ions when it dissolves:

$$CH_3COONa_{(s)} \xrightarrow{water} CH_3COO^-_{(aq)} + Na^+_{(aq)}$$

So in the solution you've got heaps of undissociated ethanoic acid molecules ($CH_3COOH_{(aq)}$), and heaps of ethanoate ions ($CH_3COO^-_{(aq)}$) from the salt.

2. Making a buffer from an excess of weak acid and some strong alkali

If you mix an excess of a weak acid with a small amount of a strong alkali then some of the acid is neutralised to make a salt, but some is left un-neutralised. The reaction mixture would then contain a weak acid and its conjugate base, and so would act as an acidic buffer.

Example

You could make an acidic buffer by mixing an excess of ethanoic acid (CH_3COOH) with sodium hydroxide (NaOH). Some of the ethanoic acid would react with the sodium hydroxide to form its conjugate base:

$$CH_3COOH + OH^- \rightleftharpoons CH_3COO^- + H_2O$$

But because the acid is in excess, some of the ethanoic acid will remain un-neutralised. This means the solution contains some ethanoic acid and some of its conjugate base, so is an acidic buffer.

Tip: When preparing buffer solutions in this way, you have to make sure the acid is in excess. If the alkali is in excess, all the acid will react and there will be no acid left.

How acidic buffers work

Whichever way you prepare an acidic buffer, the following equilibrium is set up between the weak acid and its conjugate base:

$$HA_{(aq)} \rightleftharpoons H^{+}_{(aq)} + A^{-}_{(aq)}$$

Lots of undissociated weak acid

Lots of conjugate base

The buffer solution contains lots of undissociated acid (HA), lots of the acid's conjugate base (A^-) and enough H^+ ions to make the solution acidic. When you alter the concentration of H^+ or OH^- ions in the buffer solution the equilibrium position between the conjugate pair moves to counteract the change (this is down to Le Chatelier's principle — see page 331). The conjugate base can react to mop up any excess H^+ ions, and the conjugate acid can dissociate and release H^+ ions if there's too much base around.

Figure 1: *An acidic buffer solution.*

Resisting an acid

The large number of A^- ions make the buffer able to cope with the addition of acid. If you add a small amount of acid (e.g. $HCl_{(aq)}$) the H^+ concentration increases. Most of the extra H^+ ions join with A^- ions to form HA. This shifts the equilibrium to the left, reducing the H^+ concentration to almost its original value. So the pH doesn't change much.

Resisting a base

If a small amount of base (e.g. NaOH) is added to the buffer solution, the OH^- concentration increases. Most of the extra OH^- ions react with H^+ ions to form water — removing H^+ ions from the solution. This causes more of the weak acid, HA, to dissociate to form H^+ ions — shifting the equilibrium to the right. There's no problem doing this as there's loads of spare undissociated HA molecules. The H^+ concentration increases until it's close to its original value, so the pH doesn't change much.

Example

If you mix ethanoic acid with sodium ethanoate, the following equilibrium is set up:

$$CH_3COOH_{(aq)} \rightleftharpoons H^{+}_{(aq)} + CH_3COO^{-}_{(aq)}$$

If you add some acid to this mixture, then the extra H^+ ions can react with the CH_3COO^- ions, and the equilibrium shifts to the left, reducing the H^+ concentration to almost its original value. So the pH doesn't change much.

$$\xleftarrow{\textbf{Addition of H}^{+}\textbf{ (acid)}}$$

$$CH_3COOH_{(aq)} \rightleftharpoons H^{+}_{(aq)} + CH_3COO^{-}_{(aq)}$$

If you add some base to this mixture, then the OH^- ions react with the H^+ ions to form water. This reduces the concentration of H^+, so more of the CH_3COOH molecules will dissociate to counteract this change, and the equilibrium moves to the right. This causes the H^+ concentration to rise back to almost its original value. So the pH doesn't change much.

$$\xrightarrow{\textbf{Addition of OH}^{-}\textbf{ (base)}}$$

$$CH_3COOH_{(aq)} \rightleftharpoons H^{+}_{(aq)} + CH_3COO^{-}_{(aq)}$$

Tip: CH_3COOH and CH_3COO^- are a conjugate pair. See page 337 for more on conjugate pairs.

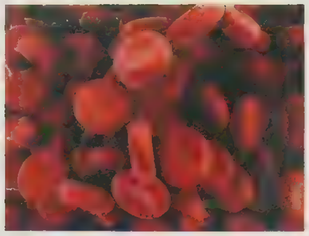


Figure 2: Red blood cells. Blood has to be kept at a pH of between 7.35 and 7.45 so is buffered by carbonic acid.

Buffer action in blood

Blood needs to be kept at between pH 7.35 and 7.45. The pH is controlled using a carbonic acid-hydrogencarbonate buffer system. Carbonic acid dissociates into H^+ ions and HCO_3^- ions as shown below:

$$H_2CO_{3(aq)} \rightleftharpoons H^+_{(aq)} + HCO_3^-{}_{(aq)}$$

If the concentration of H^+ rises in blood, then HCO_3^- ions from the carbonic acid-hydrogencarbonate buffer system will react with the excess H^+ ions, and the equilibrium will shift to the left, reducing the H^+ concentration to almost its original value. This stops the pH of blood from dropping. Meanwhile, if the concentration of H^+ ions falls in blood, then more H_2CO_3 molecules from the carbonic acid-hydrogencarbonate buffer system will dissociate, and the equilibrium will shift to the right, increasing the H^+ concentration to almost its original value. This stops the pH of blood from rising.

The levels of H_2CO_3 are controlled by respiration. By breathing out CO_2, the level of H_2CO_3 is reduced, as it moves this equilibrium to the right:

$$H_2CO_{3(aq)} \rightleftharpoons H_2O_{(l)} + CO_{2(aq)}$$

The levels of HCO_3^- are controlled by the kidneys, with excess being excreted in the urine.

Practice Questions — Fact Recall

Q1 What is a buffer?

Q2 State two ways of making an acidic buffer.

Q3 Explain how an acidic buffer resists changes in pH when:
- a) a small amount of acid is added.
- b) a small amount of base is added.

Q4 What buffer system is used to keep the pH of blood between 7.35 and 7.45?

6. Calculating the pH of Buffers

You need to be able to calculate the pH of buffer solutions. These calculations look scary, but don't worry — they're not nearly as bad as they look.

Learning Objective:

- Be able to calculate the pH of a buffer solution, from the K_a value of a weak acid and the equilibrium concentrations of the conjugate acid-base pair, and be able to calculate related quantities.

Specification Reference 5.1.3

Calculations using known concentrations

If you know the K_a of the weak acid and the equilibrium concentrations of the weak acid and its salt, calculating the pH of an **acidic buffer** isn't too tricky. To do any calculations, you need to make the following assumptions:

- The salt of the conjugate base is fully dissociated, so the equilibrium concentration of A^- is the same as the initial concentration of the salt.
- HA is only slightly dissociated, so its equilibrium concentration is the same as its initial concentration.

If these assumptions are valid, then here's how you calculate the pH of an acidic buffer:

Step 1: Write out the expression for the K_a of the weak acid.

Step 2: Rearrange the equation to give an expression for $[H^+]$.

Step 3: Substitute the value for K_a and the equilibrium concentrations of the acid and salt into the equation.

Step 4: Solve the equation to find a value for $[H^+]$.

Step 5: Substitute your value for $[H^+]$ into the pH equation ($pH = -\log_{10} [H^+]$) and solve it to calculate the pH.

Tip: Writing expressions for K_a was covered on page 346. Have a look back if you need a recap.

Example — **Maths Skills**

A buffer solution contains 0.400 mol dm^{-3} methanoic acid, HCOOH, and 0.600 mol dm^{-3} sodium methanoate, $HCOO^-Na^+$. For methanoic acid, $K_a = 1.6 \times 10^{-4}$ mol dm^{-3}. What is the pH of this buffer?

1. Write the expression for K_a of the weak acid:

$$HCOOH_{(aq)} \rightleftharpoons H^+_{(aq)} + HCOO^-_{(aq)} \quad \text{so} \quad K_a = \frac{[\mathrm{H}\ ][\mathrm{HCOO}\ ]}{[\mathrm{HCOOH}]}$$

2. Rearrange the equation to get $[H^+]$:

$$[\mathrm{H}^+] = \frac{K_a \times [\mathrm{HCOOH}]}{[\mathrm{HCOO}\ ]}$$

3. Substitute in the value of K_a and the concentrations given in the question:

From the assumptions above:

- The equilibrium concentration of $HCOO^-$ is the same as the initial concentration of $HCOO^-\ Na^+$.
- The equilibrium concentration of HCOOH is the same as its initial concentration.

$$[\mathrm{H}^+] = \frac{K_a \times [\mathrm{HCOOH}]}{[\mathrm{HCOO}^-]} = \frac{(1.6 \times 10^{-4}) \times 0.400}{0.600}$$

4. Solve to find H^+:

$$[\mathrm{H}^+] = \frac{(1.6 \times 10^{-4}) \times 0.400}{0.600} = 1.0... \times 10^{-4}\ \text{mol dm}^{-3}$$

5. Use your value of $[H^+]$ to calculate the pH:

$$\mathrm{pH} = -\log_{10} [\mathrm{H}^+] = -\log(1.0... \times 10^{-4})$$
$$= \mathbf{3.97}$$

Tip: Remember — the concentrations in the expression for K_a all have to be equilibrium concentrations.

Tip: See page 341 for a reminder on how to calculate pH.

Tip: See page 350 for more on how a buffer can be prepared by mixing an acid and a base.

Finding the equilibrium concentrations

If a buffer has been prepared by mixing an acid with a base, you might have to work out the equilibrium concentrations of the acid and its salt before you can calculate the pH. Here's what to do:

Step 1: Write out the equation for the neutralisation reaction — remember acid + base → salt + water.

Step 2: Calculate the number of moles of acid and base at the start of the reaction using the volumes and concentrations given in the question.

Step 3: Use the molar ratios in the equation to work out the moles of acid and salt left at the end of the reaction.

Step 4: Calculate the concentration of the acid and salt in the buffer solution by dividing by the volume of the solution — this is the volume of the acid and the base added together.

Step 5: Then you're ready to calculate the pH.

Tip: The molar ratios tell you how many moles of acid will react with a certain number of moles of base, and how many moles of salt are produced. These numbers will always be in the same ratio for a given reaction.

Example — Maths Skills

A buffer is formed by mixing 15 cm³ of 0.10 mol dm⁻³ sodium hydroxide (NaOH) and 30 cm³ of 0.60 mol dm⁻³ propanoic acid (CH_3CH_2COOH). Calculate the pH of this buffer solution ($K_a = 1.35 \times 10^{-5}$ mol dm⁻³).

1. Write out the equation for the reaction:

$$CH_3CH_2COOH + NaOH \rightarrow CH_3CH_2COO^-Na^+ + H_2O$$

2. Calculate the number of moles of acid and base:

$$\text{Moles } CH_3CH_2COOH = \frac{\text{Conc. (mol dm}^{-3}) \times \text{Vol. (cm}^3)}{1000} = \frac{0.60 \times 30}{1000}$$
$$= 0.018 \text{ moles}$$

$$\text{Moles NaOH} = \frac{\text{Conc. (mol dm}^{-3}) \times \text{Vol. (cm}^3)}{1000} = \frac{0.10 \times 15}{1000}$$
$$= 0.0015 \text{ moles}$$

3. The acid is in excess, so all the base reacts. There's 0.0015 moles of NaOH at the start of the reaction. If it all reacts there will be 0.0015 moles of salt at the end of the reaction.

The equation shows us that 1 mole of base will react with 1 mole of acid to give 1 mole of salt. So if there are 0.0015 moles of salt, 0.0015 moles of acid must have been used up.
This leaves 0.018 – 0.0015 = 0.0165 moles of acid.

So, the buffer solution contains 0.0015 moles of $CH_3CH_2COO^-Na^+$ and 0.0165 moles of CH_3CH_2COOH.

4. Calculate the concentration of acid and salt in the buffer solution:

The total volume of the solution is 15 + 30 = 45 cm³

$$\text{Conc. } CH_3CH_2COOH = \frac{\text{moles} \times 1000}{\text{volume (cm}^3)} = \frac{0.0165 \times 1000}{45}$$
$$= 0.37 \text{ mol dm}^{-3}$$

$$\text{Conc. } CH_3CH_2COO^-Na^+ = \frac{\text{moles} \times 1000}{\text{volume (cm}^3)} = \frac{0.0015 \times 1000}{45}$$
$$= 0.033 \text{ mol dm}^{-3}$$

Tip: It's really important that you know formulas like:

$$\text{moles} = \frac{\text{conc.} \times \text{vol. (cm}^3)}{1000}$$

You won't be able to do the harder calculations if you haven't got your head around the basics. Check out pages 544-546 for a summary of the formulas that you need to know for your A Level Chemistry exams.

5. Work out the pH as before:

$$CH_3CH_2COOH \rightleftharpoons H^+ + CH_3CH_2COO^- \text{ so } K_a = \frac{[H^+][CH_3CH_2COO^-]}{[CH_3CH_2COOH]}$$

$$[H^+] = \frac{K_a \times [CH_3CH_2COOH]}{[CH_3CH_2COO^-]} = \frac{(1.35 \times 10^{-5}) \times 0.37}{0.033}$$
$$= 1.5... \times 10^{-4} \text{ mol dm}^{-3}$$

$pH = -\log_{10}[H^+] = -\log_{10}(1.5... \times 10^{-4}) = \mathbf{3.82}$

Tip: This bit was covered in much more detail on page 353 — have a look back if you need a quick reminder of what's going on.

Practice Questions — Application

Q1 An acidic buffer solution contains 0.200 mol dm^{-3} propanoic acid (CH_3CH_2COOH) and 0.350 mol dm^{-3} potassium propanoate. For propanoic acid, $K_a = 1.35 \times 10^{-5}$ mol dm^{-3}.

a) Write an expression for the K_a of propanoic acid.

b) Calculate the concentration of H^+ ions in this buffer solution.

c) Calculate the pH of this buffer solution.

Q2 A buffer solution contains 0.150 mol dm^{-3} ethanoic acid and 0.250 mol dm^{-3} potassium ethanoate. For ethanoic acid $K_a = 1.74 \times 10^{-5}$ mol dm^{-3}. Calculate the pH of this buffer.

Q3 A buffer is made by mixing 30.0 cm^3 of 0.500 mol dm^{-3} propanoic acid (CH_3CH_2COOH) with 20.0 cm^3 of 0.250 mol dm^{-3} potassium hydroxide (KOH). For propanoic acid, $K_a = 1.35 \times 10^{-5}$ mol dm^{-3}.

a) Write an equation to show the reaction of propanoic acid with potassium hydroxide.

b) Calculate the number of moles of propanoic acid and potassium hydroxide at the beginning of the reaction.

c) Calculate the concentration of propanoic acid and potassium propanoate in the buffer solution.

d) Calculate the concentration of H^+ ions in this buffer solution.

e) Calculate the pH of the buffer solution.

Q4 A buffer is formed by mixing together 25.0 cm^3 of 0.200 mol dm^{-3} methanoic acid (HCOOH) and 15.0 cm^3 of 0.100 mol dm^{-3} sodium hydroxide (NaOH). For methanoic acid, $K_a = 1.60 \times 10^{-4}$ mol dm^{-3}. Calculate the pH of this buffer.

Learning Objectives:

- Understand the techniques and procedures used when measuring pH with a pH meter (PAG 11).
- Be able to sketch and interpret the shapes of pH titration curves for combinations of strong and weak acids with strong and weak bases.
- Be able to explain indicator colour changes in terms of equilibrium shift between the HA and A^- forms of the indicator.
- Be able to use pH titration curves to explain the choice of suitable indicators, given the pH range of the indicator.

Specification Reference 5.1.3

7. pH Curves and Titrations

When acids and bases are mixed together a neutralisation reaction occurs — H^+ ions from the acid join with OH^- ions from the base to create water. If there are equal numbers of H^+ and OH^- ions the mixture will be neutral (pH 7). What do pH curves and titrations have to do with this? Read on...

Measuring pH

PRACTICAL ACTIVITY GROUP 11

A **pH meter** does what it says on the tin — it's an electronic gadget you can use to tell you the pH of a solution (see Figure 1). pH meters have a probe that you put into your solution and a digital display that shows the reading. At the bottom of the probe is a bulb that's very delicate, so be careful when handling it.

Before you use a pH meter, you need to make sure it's calibrated correctly. Here's how you do this:

1. Place the bulb of the pH meter into distilled water and allow the reading to settle. Now adjust the reading so that it reads **7.0**.
2. Do the same with a standard solution of pH 4.0 and another of pH 10.0. Make sure you rinse the probe with distilled water in-between each reading.

You're now ready to take your actual measurement. To do this, place the probe in the liquid you're measuring and let the reading settle before you record the result. After each measurement, you should rinse the probe in distilled water.

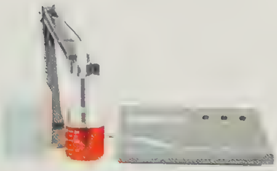
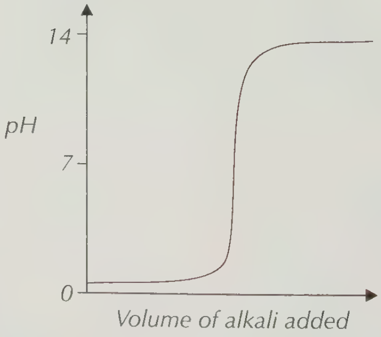


Figure 1: *A pH meter.*

pH curves

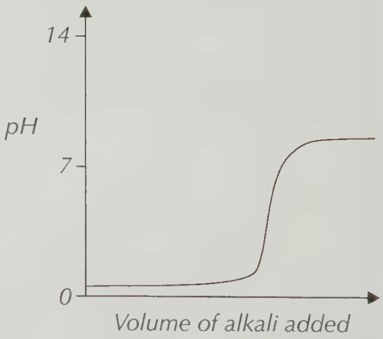
pH curves show the results of titration experiments. They can be made by plotting the pH of the titration mixture against the amount of base added as the titration goes on. The pH of the mixture can be measured using a pH meter and the scale on the burette can be used to see how much base has been added.

The shape of the curve looks a bit different depending on the strengths of the acid and base that are used. The graphs below and on the next page show the pH curves for the different combinations of strong and weak monobasic acids and bases:



Strong acid/strong base

The pH starts around 1, as there's an excess of strong acid.
It finishes up around pH 13, when you have an excess of strong base.



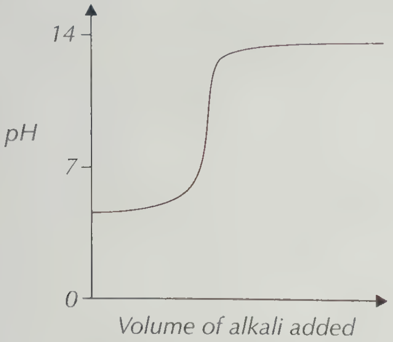
Strong acid/weak base

The pH starts around 1, as there's an excess of strong acid.
It finishes up around pH 9, when you have an excess of weak base.

Tip: If you're going to do a titration experiment, remember to carry out a risk assessment first.

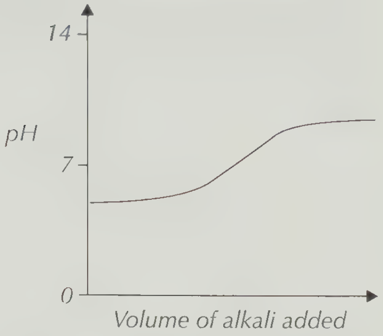
Tip: There are more details on how you can measure the pH of a solution in the Practical Skills for the Practical Endorsement section, on page 33.

Weak acid/strong base



The pH starts around 5, as there's an excess of weak acid.
It finishes up around pH 13, when you have an excess of strong base.

Weak acid/weak base



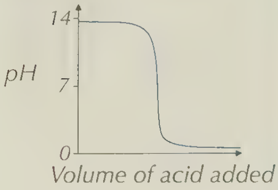
The pH starts around 5, as there's an excess of weak acid.
It finishes up around pH 9, when you have an excess of weak base.

You can explain why each graph has a particular shape:

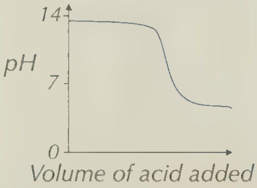
- The initial pH depends on the strength of the acid. So a strong acid titration will start at a much lower pH than a weak acid titration.
- To start with, addition of small amounts of base have little impact on the pH of the solution.
- All the graphs (apart from the weak acid/weak base graph) have a bit that's almost vertical — the mid-point of this vertical section is the equivalence point or end point. At this point $[H^+] \approx [OH^-]$ — it's here that all the acid is just neutralised. When this is the case, a tiny amount of base causes a sudden, big change in pH.
- You need to add more weak base than strong base to a strong acid to cause a pH change, and the change is less pronounced. On the other hand, you need to add less strong base to a weak acid to see a large change in pH.
- The final pH depends on the strength of the base — the stronger the base, the higher the final pH.

Tip: If you titrate a base with an acid instead, the shapes of the curves stay the same, but they're reversed. For example:

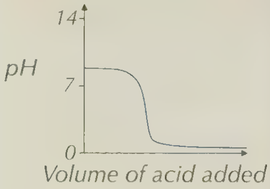
Strong base/strong acid



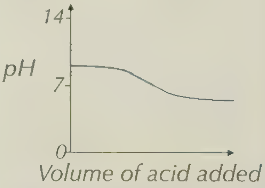
Strong base/weak acid



Weak base/strong acid



Weak base/weak acid



Indicators

You can use titrations instead of pH meters to work out the concentration of an acid or base. You'll need an **indicator** that changes colour to show you when your sample has been neutralised.

Indicators can be thought of as weak acids. They work because they have differently coloured conjugate pairs. As the pH of the solution changes during a titration, the equilibrium concentrations of the conjugate pairs will also change. The colour will change depending on whether the indicator is mainly protonated or deprotonated.

Examples

Methyl orange and **phenolphthalein** are indicators that are often used for acid-base titrations.

Phenolphthalein as an indicator

The protonated form of phenolphthalein is colourless, whilst its conjugate base is pink:

$$\underset{\text{colourless}}{\text{Phenolphthalein-H}} \rightleftharpoons \underset{\text{pink}}{\text{Phenolphthalein}^-} + H^+$$

Tip: Have a look back at page 87 if you're not sure how to calculate the concentration of an acid or base from titration data.

At low pH, there are lots of H^+ ions in solution, so most of the phenolphthalein is protonated and the indicator is colourless. As the pH rises, and the concentration of H^+ ions decreases, the equilibrium shifts to the right, and more of the phenolphthalein deprotonates. So, at high pH, the indicator is pink.

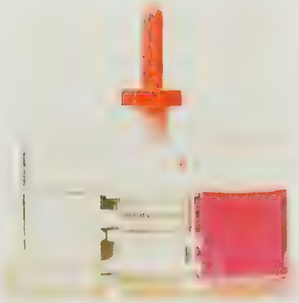


Figure 2: *The colourless to pink colour change of phenolphthalein.*

Methyl orange as an indicator

The protonated form of methyl orange is red, whilst its conjugate base is yellow:

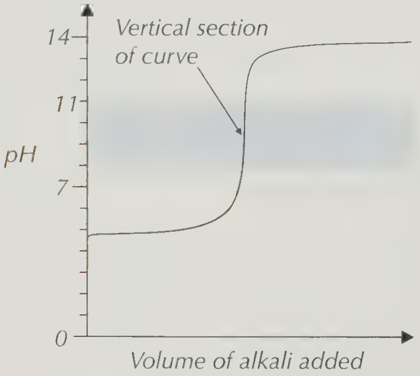
$$\underset{\text{red}}{\text{Methyl orange-H}} \rightleftharpoons \underset{\text{yellow}}{\text{Methyl orange}^-} + H^+$$

At low pH, there are lots of H^+ ions in solution, so most of the methyl orange is protonated and the indicator is red. As the pH rises, and the concentration of H^+ ions decreases, the equilibrium shifts to the right, and more of the methyl orange deprotonates. At high pH, the indicator is yellow.

Figure 3: *The red to yellow colour change of methyl orange.*

Choosing indicators

When you use an indicator, you need it to change colour exactly at the end point of your titration. So you need to pick one that changes colour over a narrow pH range that lies entirely on the vertical part of the pH curve. So for the titration shown in Figure 4 (below) you'd want an indicator that changed colour somewhere between pH 8 and pH 11:



The curve is vertical between pH 8 and pH 11— so a very small amount of alkali will cause the pH to change from 8 to 11.

So, an indicator that changes colour between pH 8 and pH 11 is needed.

Figure 4: *Graph showing how to select an indicator.*

Methyl orange and phenolphthalein each change colour over a different pH range:

Name of indicator	Colour at low pH	Approx. pH of colour change	Colour at high pH
Methyl orange	red	3.1 – 4.4	yellow
Phenolphthalein	colourless	8.3 – 10	pink

- For a strong acid/strong alkali titration, you can use either of these indicators — there's a rapid pH change over the range for both indicators.
- For a strong acid/weak alkali only methyl orange will do. The pH changes rapidly across the range for methyl orange, but not for phenolphthalein.
- For a weak acid/strong alkali, phenolphthalein is the stuff to use. The pH changes rapidly over phenolphthalein's range, but not over methyl orange's.
- For weak acid/weak alkali titrations there's no sharp pH change, so no indicator will work.

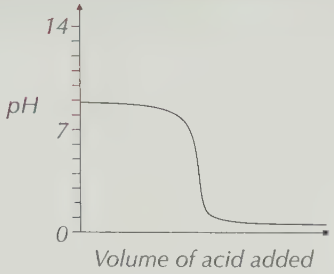
Exam Tip
Don't worry, you don't have to learn the pH ranges of any indicators. You'll always be told them in the question if you need to use them.

Tip: To find the end point of a weak acid/weak base titration, you can't use an indicator — you have to use a pH meter instead.

You need to be able to use a pH curve to explain a choice of indicator:

Example — Maths Skills

The graph to the right shows the pH curve produced when a strong acid is added to a weak base. Bromophenol blue, which has a pH range of 3.0 – 4.6, was used as an indicator. Explain why bromophenol blue is a suitable indicator to use.



The graph shows that the vertical part of the pH curve is between about pH 2 and pH 6. So you need an indicator with a pH range between 2 and 6. Bromophenol blue changes colour within this range so bromophenol blue is a suitable indicator to choose.

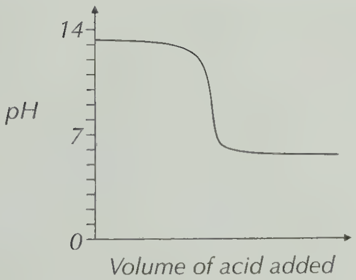
Tip: The pH range of an indicator is the range in which the colour changes.

Practice Questions — Application

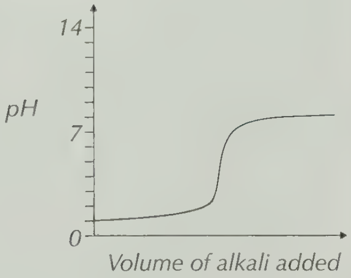
Q1 The graphs below show the pH curves for four different acid–base titrations. For each reaction state what type of acid and base were used and select an appropriate indicator from the table below.

Indicator	pH range
Thymol blue	1.2 – 2.8
Methyl orange	3.1 – 4.4
Litmus	5.0 – 8.0
Cresol purple	7.6 – 9.2
Phenolphthalein	8.3 – 10

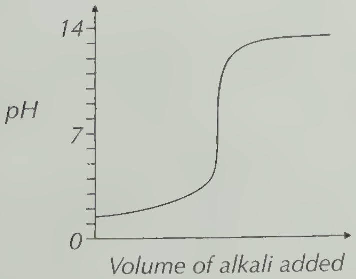
a)



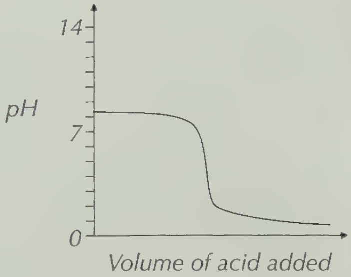
b)



c)



d)



Tip: You need to look at where the curves start and finish to work out if you've got an acid neutralising a base or a base neutralising an acid.

Q2 Neutral red changes colour from red to yellow between pH 6.8 and pH 8.0. Sketch the pH curve for a titration reaction that this indicator could be used for.

Practice Questions — Fact Recall

Q1 Sketch the pH curve produced when:
  a) A strong acid neutralises a weak base.
  b) A strong base neutralises a strong acid.
  c) A weak acid neutralises a strong base.

Q2 a) What happens at the end point of a titration reaction?
  b) How can you see that the end point has been reached when you're carrying out a titration?
  c) How can you tell the end point has been reached using a pH curve?

Q3 How would you know if an indicator is suitable for a particular titration reaction?

Tip: Don't forget — acids have low pHs and bases have high pHs.

Section Summary

Make sure you know...

- That a Brønsted-Lowry acid is a species that can donate a proton and a Brønsted-Lowry base is a species that can accept a proton.
- That strong acids/bases dissociate fully in water while weak acids/bases only partially dissociate.
- That monobasic acids donate one proton per molecule into solution, dibasic acids can donate two protons per molecule and tribasic acids can donate three protons per molecule into solution.
- What conjugate acid-base pairs are and how to identify them.
- How acids react with metals, carbonates, alkalis and metal oxides.
- That $pH = -\log_{10} [H^+]$ where $[H^+]$is the concentration of H^+ ions in mol dm^{-3}.
- How to convert pH into $[H^+]$ and vice versa.
- How to calculate the pH of a strong, monobasic acid from its concentration, or calculate its concentration from the pH.
- That water is weakly dissociated and the ionic product of water is $K_w = [H^+][OH^-]$.
- How to calculate the pH of a strong base from its concentration and vice versa, using K_w.
- That K_a is the dissociation constant for a weak acid, and how to write expressions for K_a.
- How to calculate the pH of a weak acid from its concentration and K_a.
- How to calculate the concentration of a weak acid from its pH and K_a.
- How to calculate K_a for a weak acid from its pH and concentration.
- That $pK_a = -\log_{10} (K_a)$ and how to convert K_a to pK_a and vice versa.
- That K_w and K_a are both equilibrium constants, so are both constant at constant temperature.
- The effect on K_w and K_a of changing the temperature for exothermic and endothermic dissociation.
- How K_w and K_a control the position of equilibrium for dissociation on changing the concentrations of H^+, OH^- or A^-, and on changing temperature.
- What a buffer is, how to make one and how an acidic buffer can resist changes in pH.
- The role of the carbonic acid-hydrogencarbonate buffer system in maintaining blood pH.
- How to calculate the pH of an acidic buffer and related quantities.
- How to measure pH using a pH meter.
- What the pH curves for all the different combinations of weak and strong acids and bases look like.
- That indicators change colour due to changes in the equilibrium between the differently coloured HA and A^- forms of the indicator.
- How to use pH curves to select an appropriate pH indicator to use in a titration.

Exam-style Questions

1 A 0.375 mol dm^{-3} solution of lactic acid, a weak acid, has a pH of 2.14 at 25 °C. What is K_a of lactic acid at this temperature?

- **A** 0.019 mol dm^{-3}
- **B** 1.4×10^{-4} mol dm^{-3}
- **C** 3.85
- **D** 7.24×10^{-3} mol dm^{-3}

(1 mark)

2 What is the pH of a 0.012 mol dm^{-3} solution of the strong base potassium hydroxide, KOH, at 15 °C? K_w at this temperature is 0.457×10^{-14} mol^2 dm^{-6}.

- **A** 7.17
- **B** 14.34
- **C** 1.82
- **D** 12.42

(1 mark)

3 Methanoic acid (HCOOH) is a weak acid. A 0.240 mol dm^{-3} solution of HCOOH has a pH of 2.18 at 25 °C.

(a) (i) Write out the equation for the dissociation of HCOOH.

(1 mark)

(ii) Write out an expression for K_a for this acid.

(1 mark)

(iii) Calculate the pK_a of methanoic acid at 25 °C.

(3 marks)

(b) A buffer solution contains 0.0840 mol dm^{-3} methanoic acid (HCOOH) and 0.0600 mol dm^{-3} ammonium methanoate ($HCOONH_4$)

(i) Calculate the pH of this buffer.

(2 marks)

(ii) This buffer can be prepared by reacting methanoic acid with ammonia.

- Write an equation for the reaction of methanoic acid with ammonia.
- Label one conjugate acid/base pair 'Acid 1' and 'Base 1'.
- Label the other conjugate acid/base pair 'Acid 2' and 'Base 2'.

(3 marks)

(iii) Explain how this buffer resists changes in pH when an acid is added.

(3 marks)

4 The concentrations of strong acids and strong bases can be found by carrying out titrations. Titrations are usually done at room temperature (25.0 °C). The value of K_w at 25.0 °C is 1.00×10^{-14} mol dm^{-3}.

(a) (i) Give the expression for K_w.

(1 mark)

(ii) Give the expression for pH.

(1 mark)

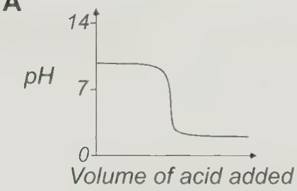
(b) Calculate the pH of a 0.150 mol dm^{-3} solution of NaOH at 25.0 °C.

(3 marks)

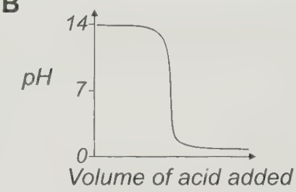
(c) In a titration reaction at 25.0 °C, 25.0 cm^3 of this 0.150 mol dm^{-3} solution of NaOH was neutralised by 18.5 cm^3 of a 0.203 mol dm^{-3} solution of HCl.

(i) Which of the graphs below (A, B and C) shows the pH curve for this reaction?

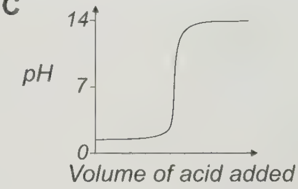
A



B



C

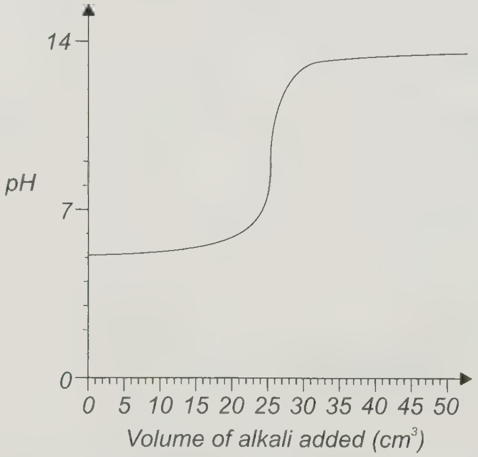


(1 mark)

(ii) Calculate the pH of the HCl solution.

(2 marks)

(d) The pH curve for another titration is shown below.



Indicator	pH range
Thymol blue	1.2 – 2.8
Bromophenol blue	3.0 – 4.6
Litmus	5.0 – 8.0
Phenolphthalein	8.3 – 10

(i) Suggest an acid and a base that could have been used in this titration.

(2 marks)

(ii) From the table above, suggest an indicator that would be suitable for this titration.

(1 mark)

1. Enthalpy Changes

Some of this stuff may ring a few bells from Module 3: Section 2. Make sure you understand all the definitions in this topic because they're really important for the rest of the section.

The basics

Enthalpy notation

Enthalpy change, ΔH (delta H), is the heat energy transferred in a reaction at constant pressure. The units of ΔH are kJ mol^{-1}. You write ΔH° to show that the substances were in their standard states and that the measurements were made under **standard conditions**. Standard conditions are 100 kPa (about 1 atm) pressure and a stated temperature (e.g. ΔH°_{298}). In this book, all the enthalpy changes are measured at 298 K (25 °C). Sometimes the notation will also include a subscript, for example to signify whether the enthalpy change is for a reaction (r), for combustion (c), or for the formation of a new compound (f).

Tip: You covered enthalpy notation on page 166.

Exothermic and endothermic reactions

Exothermic reactions have a negative ΔH value, because heat energy is given out (the chemicals lose energy). **Endothermic reactions** have a positive ΔH value, because heat energy is absorbed (the chemicals gain energy).

Tip: HOW SCIENCE WORKS According to the first law of thermodynamics, energy is always conserved (it is never created or destroyed). So if the products of a reaction have less energy than the reactants, the extra energy has to go somewhere. It is transferred to the surroundings as heat energy — this is the enthalpy change.

Enthalpy and energy definitions

There are lots of different enthalpy and energy terms you need to know on the next few pages. Unfortunately, each specific type of change has its own definition and you need to learn them all.

- **Enthalpy change of formation**, $\Delta_f H$, is the enthalpy change when 1 mole of a compound is formed from its elements, e.g. $Ca_{(s)} + Cl_{2(g)} \rightarrow CaCl_{2(s)}$
- **Enthalpy change of atomisation of an element**, $\Delta_{at} H$, is the enthalpy change when 1 mole of gaseous atoms is formed from an element, e.g. $\frac{1}{2}Cl_{2(g)} \rightarrow Cl_{(g)}$
- **Enthalpy change of atomisation of a compound**, $\Delta_{at} H$, is the enthalpy change when 1 mole of a compound is converted to gaseous atoms, e.g. $NaCl_{(s)} \rightarrow Na_{(g)} + Cl_{(g)}$
- The **first ionisation energy** is the energy needed to change 1 mole of gaseous atoms into 1 mole of gaseous 1+ ions, e.g. $Mg_{(g)} \rightarrow Mg^{+}_{(g)} + e^{-}$
- The **second ionisation energy** is the energy needed to change 1 mole of gaseous 1+ ions atoms into 1 mole of gaseous 2+ ions, e.g. $Mg^{+}_{(g)} \rightarrow Mg^{2+}_{(g)} + e^{-}$
- **First electron affinity** is the energy needed to change 1 mole of gaseous atoms into 1 mole of gaseous 1– ions, e.g. $O_{(g)} + e^{-} \rightarrow O^{-}_{(g)}$
- **Second electron affinity** is the energy needed to change 1 mole of gaseous 1– ions into 1 mole of gaseous 2– ions, e.g. $O^{-}_{(g)} + e^{-} \rightarrow O^{2-}_{(g)}$

Exam Tip
You'll have to understand all of these definitions for the exam, so make sure you've learned them all.

Tip: There's lots more on lattice enthalpy on page 365, and more on enthalpy change of hydration and enthalpy change of solution on page 371.

- **Lattice enthalpy**, $\Delta_{LE}H$, is the enthalpy change when 1 mole of a solid ionic compound is formed from its gaseous ions, e.g. $Na^+_{(g)} + Cl^-_{(g)} \rightarrow NaCl_{(s)}$
- The **enthalpy change of hydration**, $\Delta_{hyd}H$, is the enthalpy change when 1 mole of gaseous ions is dissolved in water, e.g. $Na^+_{(g)} \rightarrow Na^+_{(aq)}$
- The **enthalpy change of solution**, $\Delta_{sol}H$, is the enthalpy change when 1 mole of solute is dissolved in a solvent, such as water, e.g. $NaCl_{(s)} \rightarrow NaCl_{(aq)}$

Tip: These terms will crop up a lot in this section so don't move on until you understand what each one means — you might want to fold this page over so you can find it again if you need to.

Practice Questions — Fact Recall

Q1 What is meant by the term enthalpy change?

Q2 Give the symbol for enthalpy change.

Q3 Define the following:
  a) enthalpy change of formation,
  b) second electron affinity,
  c) enthalpy change of hydration.

Q4 Name the enthalpy or energy changes defined below:
  a) The enthalpy change when 1 mole of gaseous atoms is formed from an element.
  b) The energy needed to change 1 mole of gaseous atoms into 1 mole of gaseous 1– ions.

Q5 Write the symbol for the following enthalpy changes:
  a) the enthalpy change of hydration,
  b) the enthalpy change of solution.

2. Lattice Enthalpy

As you might have guessed from the title, this topic is all about lattice enthalpies. Read on to find out what lattice enthalpies are, why they are useful and what affects the lattice enthalpy of an ionic compound.

What is lattice enthalpy?

Ionic compounds can form regular structures called giant ionic lattices, where the positive and negative ions are held together by electrostatic attractions. When gaseous ions combine to make a solid ionic lattice, energy is given out — this is called the **lattice enthalpy**. So, lattice enthalpy is a measure of ionic bond strength. Here's the definition of lattice enthalpy that you need to know:

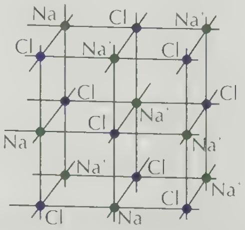
> The **lattice enthalpy**, $\Delta_{LE}H$, is the enthalpy change when 1 mole of a solid ionic lattice is formed from its gaseous ions.

Example

Sodium chloride (NaCl) is an example of an ionic lattice. The diagram below shows how NaCl is formed from gaseous Na^+ and Cl^- ions.

$$Na^+_{(g)} + Cl^-_{(g)} \longrightarrow$$

Gaseous sodium and chloride ions come together...



... to form a solid ionic lattice of sodium chloride.

The standard lattice enthalpy, $\Delta_{LE}H^\circ$, for this reaction is –787 kJ mol^{-1}. The negative ΔH value shows that lattice formation is an exothermic process.

Lattice enthalpies are quite handy because they tell you how strong the ionic bonding is. The more negative the lattice enthalpy, the stronger the bonding.

Example

The lattice enthalpies of NaCl and MgO are:

$$Na^+_{(g)} + Cl^-_{(g)} \rightarrow NaCl_{(s)} \qquad \Delta_{LE}H^\circ = -787 \text{ kJ mol}^{-1}$$
$$Mg^{2+}_{(g)} + O^{2-}_{(g)} \rightarrow MgO_{(s)} \qquad \Delta_{LE}H^\circ = -3791 \text{ kJ mol}^{-1}$$

Out of NaCl and MgO, MgO has the more negative lattice enthalpy so the MgO lattice is held together by stronger ionic bonds.

Factors affecting lattice enthalpy

Lattice enthalpies have specific values that differ depending on the ions involved. There are two main factors which influence the lattice enthalpy:

1. Ionic charge

The higher the charges on the ions, the stronger the electrostatic attractions between the ions so the more energy is released when an ionic lattice forms. More energy released means that the lattice enthalpy will be more negative. So the lattice enthalpies for compounds with 2+ or 2– ions (e.g. Mg^{2+} or S^{2-}) are more negative than those with 1+ or 1– ions (e.g. Na^+ or Cl^-).

Learning Objectives:

- Be able to explain the term lattice enthalpy (formation of 1 mole of ionic lattice from gaseous ions, $\Delta_{LE}H$) and know that it is used as a measure of the strength of ionic bonding in a giant ionic lattice.
- Be able to give a qualitative explanation of the effect of ionic charge and ionic radius on the exothermic value of a lattice enthalpy.

Specification Reference 5.2.1

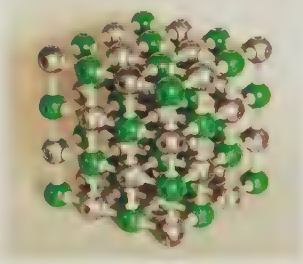


Figure 1: *A 3D model of a sodium chloride lattice.*

Tip: Ionic compounds with two 1+ (or 1–) ions and one 2– (or 2+) ion, like Na_2O, have intermediate lattice enthalpies.

Tip: You can work out the charge on an ion from the periodic table — elements in Group 1 form 1+ ions, elements in Group 2 form 2+ ions, elements in Group 6 form 2– ions and elements in Group 7 form 1– ions.

Example

The standard lattice enthalpy of NaCl is only –787 kJ mol^{-1}, but the standard lattice enthalpy of $MgCl_2$ is –2526 kJ mol^{-1}.

MgS has an even higher standard lattice enthalpy (–3299 kJ mol^{-1}) because both magnesium and sulfur ions have double charges.

2. Ionic radius

The smaller the ionic radii of the ions involved, the higher the charge density of the ion. This means the electrostatic attraction between the ions is greater so the lattice enthalpy is more exothermic (more negative).

Example

Here are the standard lattice enthalpies of some chloride compounds:

Compound	*Standard lattice enthalpy (kJ mol^{-1})*
LiCl	*–861*
NaCl	*–787*
KCl	*–701*
RbCl	*–692*

Of all the positive ions, Li^+ has the smallest ionic radius. This means that LiCl has the most exothermic lattice enthalpy because the smaller Li^+ ions are more strongly attracted to the Cl^- ions than larger ions like Rb^+.

Tip: Li, Na, K and Rb are all in Group 1 of the periodic table.

You should remember from Module 3: Section 1 that ionic radius increases down a group — so have a look at the periodic table if you're unsure about which ions have the largest ionic radii.

Exam Tip

Don't worry — you don't need to remember any of these standard lattice enthalpy values. You'll always be told them in the exam if you need to use them.

Exam Tip

In the exam, you need to be able to explain why one ionic compound has a higher or lower lattice enthalpy than another ionic compound — so make sure you understand why these two factors affect the standard lattice enthalpy.

Practice Questions — Application

Q1 The table below shows the standard lattice enthalpies of some sodium containing compounds.

Compound	*Standard lattice enthalpy (kJ mol^{-1})*
NaCl	*–787*
NaBr	*–747*
NaI	*–704*

a) Explain why the standard lattice enthalpy becomes less exothermic from NaCl to NaI.

b) Which of these compounds contains the strongest ionic bonds?

Q2 The standard lattice enthalpy of K_2O is –2238 kJ mol^{-1}. Would you expect the standard lattice enthalpy of CaO to be more or less negative than this? Explain your answer.

Practice Questions — Fact Recall

Q1 a) Define the term 'lattice enthalpy'.

b) What is the symbol for lattice enthalpy?

Q2 What is the relationship between the lattice enthalpy of an ionic compound and the ionic bond strength?

Q3 Name two factors that affect the lattice enthalpy of an ionic compound.

3. Born-Haber Cycles

Get those rulers and pencils out — it's time to draw some Born-Haber cycles.

Forming ionic lattices

The lattice enthalpy is the enthalpy change when an ionic lattice is formed from its gaseous ions. But when an ionic lattice forms, you won't usually start with gaseous ions — you'll probably start with elements in their standard states. There are two routes you can follow to get from the elements in their standard states to an ionic lattice:

- A direct route, which involves converting the elements in their standard states directly into an ionic lattice. The enthalpy change for this reaction is given by the enthalpy of formation ($\Delta_f H$) of the lattice.
- An indirect route, which involves forming gaseous atoms, converting these into gaseous ions and then forming the ionic lattice. Each of the steps in this route has its own energy change — see Figure 1.

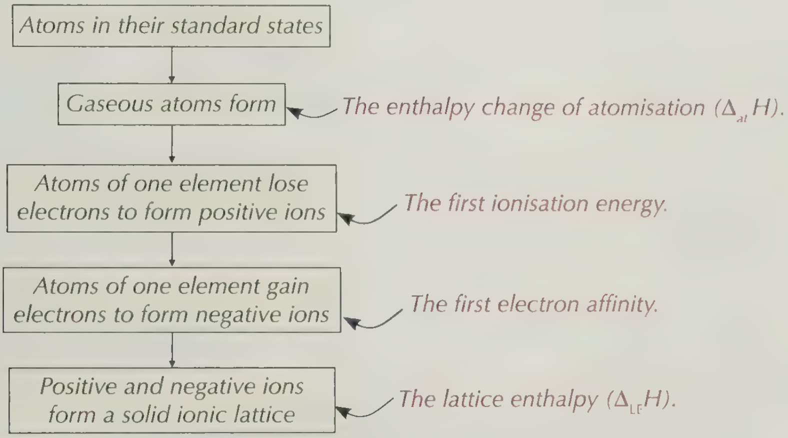
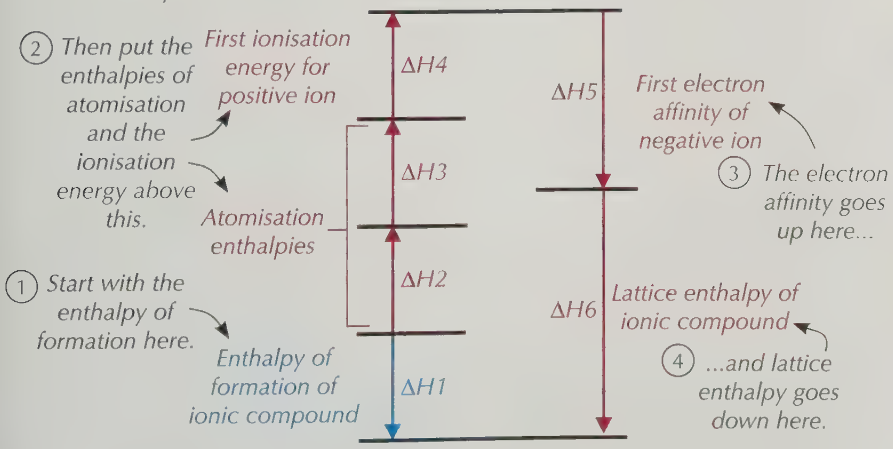

Atoms in their standard states
Gaseous atoms form
The enthalpy change of atomisation ($\Delta_{at} H$).
Atoms of one element lose electrons to form positive ions
The first ionisation energy.
Atoms of one element gain electrons to form negative ions
The first electron affinity.
Positive and negative ions form a solid ionic lattice
The lattice enthalpy ($\Delta_{LE}H$).

Figure 1: *The indirect route for forming an ionic lattice.*

Born-Haber cycles

The two different routes for forming an ionic lattice and the energy changes involved can be illustrated using a **Born-Haber cycle**. Here's how to draw a Born-Haber cycle:


② Then put the enthalpies of atomisation and the ionisation energy above this.
First ionisation energy for positive ion
Atomisation enthalpies
① Start with the enthalpy of formation here.
Enthalpy of formation of ionic compound
ΔH4
ΔH3
ΔH2
ΔH1
ΔH5
ΔH6
First electron affinity of negative ion
③ The electron affinity goes up here...
Lattice enthalpy of ionic compound
④ ...and lattice enthalpy goes down here.

On the diagram above, the blue arrow shows the direct route and the red arrows show the indirect route.

Learning Objective:

- Be able to use the lattice enthalpy of a simple ionic solid (e.g. NaCl, $MgCl_2$) and relevant energy terms to construct Born–Haber cycles and carry out related calculations.

Specification Reference 5.2.1

Tip: See pages 363-364 for a recap on the definitions of all these different energy changes.

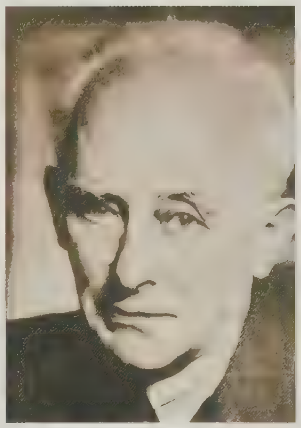


Figure 2: *German physicist, Max Born, who, along with Fritz Haber, developed Born-Haber cycles.*

Tip: The Haber who helped develop Born-Haber cycles is the same Haber who invented the Haber process for synthesising ammonia.

Figure 3: *Victor Franz Hess — the scientist who proposed Hess's law.*

Tip: You can use this technique to find any unknown enthalpy change on the diagram, as long as you know all the rest — just use an alternative route round the diagram.

Tip: Don't forget — ΔH is the symbol for enthalpy change. See page 363 for more.

Tip: You can also get the equation above by re-arranging this equation:
$\Delta H1 = \Delta H2 + \Delta H3 + \Delta H4 + \Delta H5 + \Delta H6$.

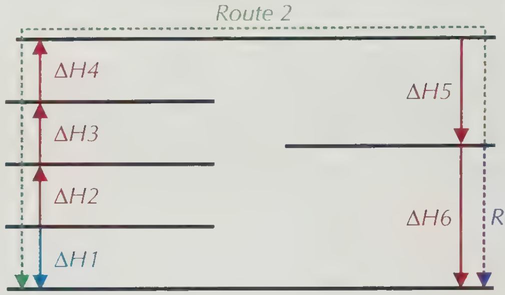
Tip: Be really careful with your + and – signs in these calculations. You could end up minusing a minus number which is the same as adding it.

Calculating lattice enthalpies using Born-Haber cycles

Lattice enthalpies can't be measured directly, but **Hess's law** states that:

> The total enthalpy change of a reaction is always the same, no matter which route is taken.

This means that if you know all the other enthalpy changes, you can use a Born-Haber cycle to calculate the lattice enthalpy via an indirect route. All you have to do is use an alternative route around the diagram — for example, route 2 on the diagram below:


Route 2
ΔH4
ΔH3
ΔH2
ΔH1
ΔH5
ΔH6
Route 1

According to Hess's law, the enthalpy change of route 1 (the lattice enthalpy) is the same as the enthalpy change of route 2.

You can find the ΔH of route 2 by adding all the enthalpy changes in this route together and adding in a minus sign whenever you go the wrong way along an arrow. So...

$$\Delta H_{\text{route 2}} = (-\Delta H5) + (-\Delta H4) + (-\Delta H3) + (-\Delta H2) + \Delta H1$$

Add all the enthalpy changes in route 2 together.

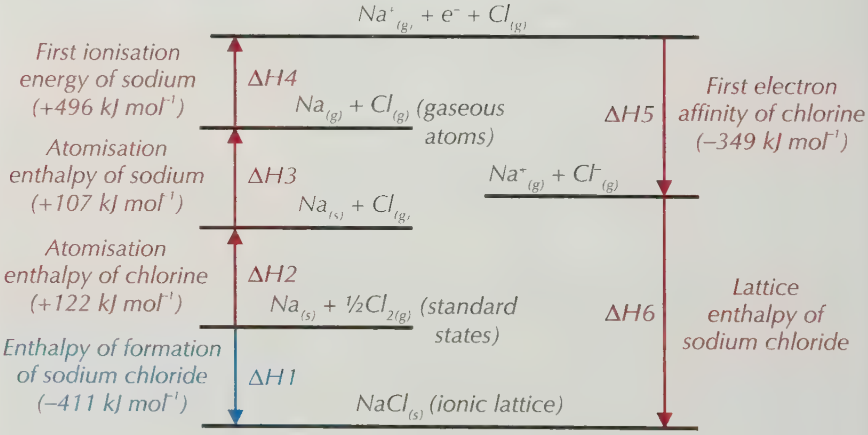
Add a minus sign if you go the wrong way along an arrow.

$$\Delta H_{\text{route 2}} = \Delta H_{\text{route 1}} = \Delta H6 \text{ so...}$$

$$\Delta H6 = -\Delta H5 - \Delta H4 - \Delta H3 - \Delta H2 + \Delta H1$$

Example — **Maths Skills**

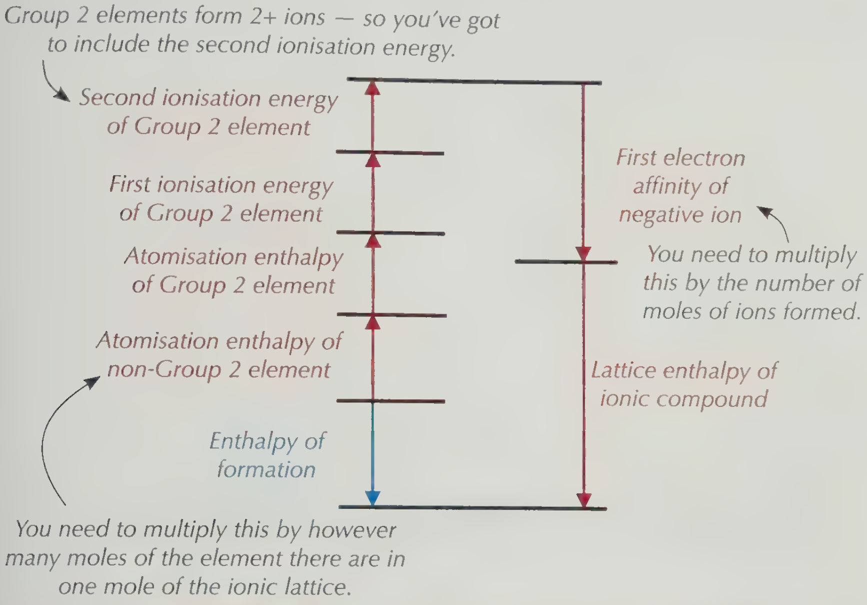
This is the Born-Haber cycle for the formation of sodium chloride:


$Na^+_{(g)} + e^- + Cl_{(g)}$
First ionisation energy of sodium (+496 kJ mol^{-1})
ΔH4
$Na_{(g)} + Cl_{(g)}$ (gaseous atoms)
ΔH5
First electron affinity of chlorine (–349 kJ mol^{-1})
Atomisation enthalpy of sodium (+107 kJ mol^{-1})
ΔH3
$Na^+_{(g)} + Cl^-_{(g)}$
$Na_{(s)} + Cl_{(g)}$
Atomisation enthalpy of chlorine (+122 kJ mol^{-1})
ΔH2
$Na_{(s)} + \frac{1}{2}Cl_{2(g)}$ (standard states)
ΔH6
Lattice enthalpy of sodium chloride
Enthalpy of formation of sodium chloride (–411 kJ mol^{-1})
ΔH1
$NaCl_{(s)}$ (ionic lattice)

Hess's law says that the total enthalpy change of a reaction is always the same, no matter which route is taken. So...

$$\Delta_{LE}H = \Delta H6 = -\Delta H5 - \Delta H4 - \Delta H3 - \Delta H2 + \Delta H1$$
$$= -(-349) - (+496) - (+107) - (+122) + (-411) = \mathbf{-787\ kJ\ mol^{-1}}$$

Born-Haber cycles for compounds containing Group 2 elements have a few changes from the ones on the previous page. Here's a Born-Haber cycle for a compound containing a Group 2 element:


Group 2 elements form 2+ ions — so you've got to include the second ionisation energy.
Second ionisation energy of Group 2 element
First ionisation energy of Group 2 element
Atomisation enthalpy of Group 2 element
Atomisation enthalpy of non-Group 2 element
Enthalpy of formation
You need to multiply this by however many moles of the element there are in one mole of the ionic lattice.
First electron affinity of negative ion
You need to multiply this by the number of moles of ions formed.
Lattice enthalpy of ionic compound

Exam Tip
Make sure you understand what's going on with these Group 2 elements so you can handle whatever compound they throw at you in the exam.

Tip: Remember, enthalpy change of formation, $\Delta_f H$, is the enthalpy change when one mole of a compound is formed from its elements.

Example **Maths Skills**

Magnesium can react with chlorine to form magnesium chloride. Here's how you calculate the lattice enthalpy of magnesium chloride ($MgCl_2$).

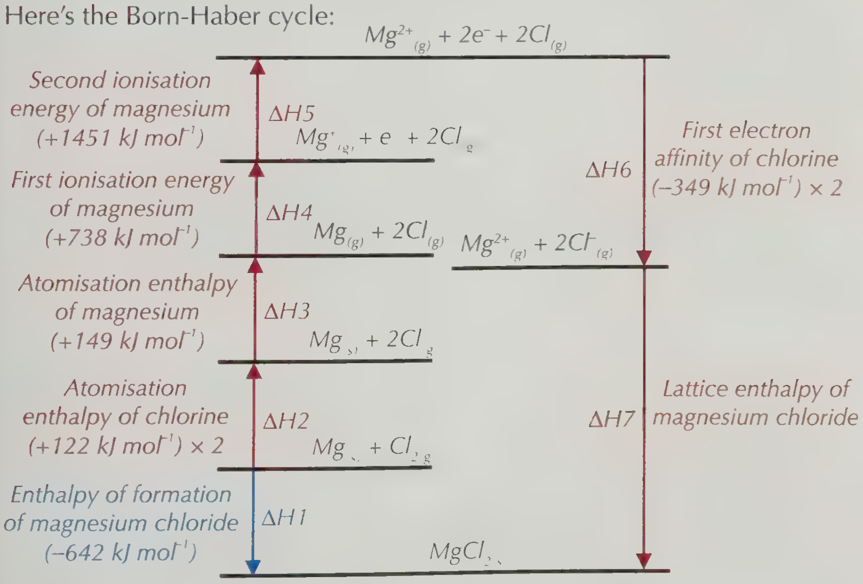
$$Mg_{(g)} + Cl_{2(g)} \rightarrow MgCl_{2(s)}$$

Magnesium forms 2+ ions — so you've got to include the second ionisation energy.

You need to multiply the electron affinity of chlorine by 2 because two moles of ions form.

You need to multiply the atomisation enthalpy of chlorine by 2 because there are two moles of Cl in one mole of $MgCl_2$.

Here's the Born-Haber cycle:


Mg2+(g) + 2e− + 2Cl(g)
Second ionisation energy of magnesium (+1451 kJ mol−1)
ΔH5
Mg+(g) + e− + 2Cl(g)
First ionisation energy of magnesium (+738 kJ mol−1)
ΔH4
Mg(g) + 2Cl(g)
Atomisation enthalpy of magnesium (+149 kJ mol−1)
ΔH3
Mg(s) + 2Cl(g)
Atomisation enthalpy of chlorine (+122 kJ mol−1) × 2
ΔH2
Mg(s) + Cl2(g)
Enthalpy of formation of magnesium chloride (−642 kJ mol−1)
ΔH1
MgCl2(s)
ΔH6
First electron affinity of chlorine (−349 kJ mol−1) × 2
Mg2+(g) + 2Cl−(g)
ΔH7
Lattice enthalpy of magnesium chloride

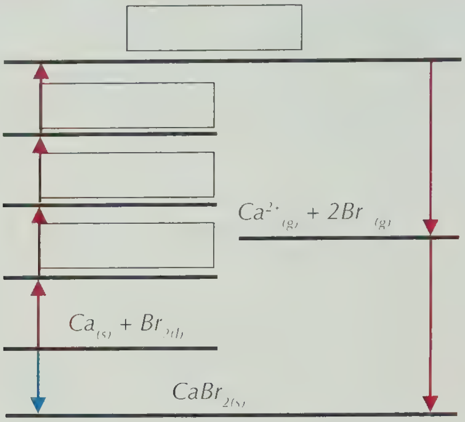
$$\Delta_{LE}H = \Delta H7 = -\Delta H6 - \Delta H5 - \Delta H4 - \Delta H3 - \Delta H2 + \Delta H1$$
$$= -(-349 \times 2) - (+1451) - (+738) - (+149) - (+122 \times 2) + (-642)$$
$$= \mathbf{-2526\ kJ\ mol^{-1}}$$

Figure 4: *Dry magnesium chloride.*

Tip: State symbols are really important here. If you're not sure of which state symbols go with which steps, check the definitions on pages 363-364.

Practice Questions — Application

Q1 Complete the following Born-Haber cycle for the formation of $CaBr_2$.



Q2 Look at the table below.

Enthalpy change	*ΔH° / kJ mol^{-1}*
Enthalpy change of atomisation of chlorine	*+122*
Enthalpy change of atomisation of lithium	*+159*
First ionisation energy of lithium	*+520*
First electron affinity of chlorine	*–349*
Lattice enthalpy of lithium chloride	*–861*

a) Draw the Born-Haber cycle for the formation of LiCl.

b) Use Hess's law to calculate the enthalpy of formation of LiCl.

Q3 Look at the table below.

Enthalpy change	*ΔH° / kJ mol^{-1}*
Enthalpy change of atomisation of potassium	*+89*
Enthalpy change of atomisation of fluorine	*+79*
First ionisation energy of potassium	*+419*
First electron affinity of fluorine	*–328*
Enthalpy of formation of potassium fluoride	*–563*

a) Draw the Born-Haber cycle for the formation of KF.

b) Use Hess's law to calculate the lattice enthalpy of KF.

Exam Tip
If you're asked to complete a Born-Haber cycle, it just means fill in the blank bits on the diagram — you don't have to write out what each stage is unless it specifically asks you to.

Tip: Calcium is a Group 2 element.

Exam Tip
Always double-check that you've got the plus and minus signs right when you're doing calculations using a Born-Haber cycle. It's really easy to make a mistake and get it wrong in the exam — and you will lose precious marks.

Exam Tip
When completing Born-Haber cycles in the exam, make sure you get the enthalpy changes in the right order. Atomisation always comes before ionisation, and they always come before electron affinity.

4. Enthalpies of Solution

Lattice enthalpies aren't the only enthalpies you can calculate using Hess's law. You can work out enthalpies of solution too. You'll need to remind yourself of the definition of lattice enthalpy (page 365) before you start.

Dissolving ionic lattices

When a solid ionic lattice dissolves in water these two things happen:

- The bonds between the ions break to give gaseous ions — this is endothermic. This enthalpy change is the opposite of the **lattice enthalpy**.
- Bonds between the ions and the water are made — this is exothermic. The enthalpy change here is called the **enthalpy change of hydration**.

Water can form bonds with the ions because it is a polar molecule. Oxygen is more electronegative than hydrogen, so it draws the bonding electrons toward itself, creating a dipole. Consequently, positive ions form weak bonds with the partial negative charge on the oxygen atom and negative ions form weak bonds with the partial positive charge on the hydrogen atoms (see Figure 1).

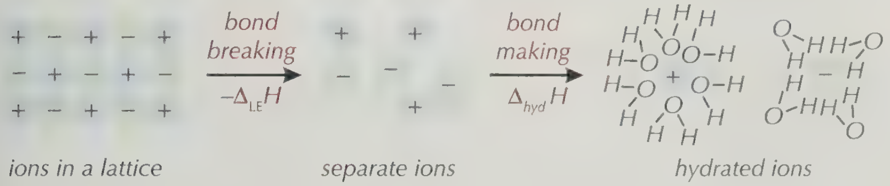


Figure 1: *A solid ionic lattice dissolving in water.*

The **enthalpy change of solution** is the overall effect on the enthalpy of bond breaking and bond making. Here are the definitions you need to know:

> The **enthalpy change of hydration**, $\Delta_{hyd}H$, is the enthalpy change when 1 mole of gaseous ions is dissolved in water, e.g. $Na^+_{(g)} \rightarrow Na^+_{(aq)}$

> The **enthalpy change of solution**, $\Delta_{sol}H$, is the enthalpy change when 1 mole of solute is dissolved in a solvent, such as water, e.g. $NaCl_{(s)} \rightarrow NaCl_{(aq)}$

Entropy and dissolving ionic lattices

Substances generally only dissolve if the energy released is roughly the same, or greater than the energy taken in. But enthalpy change isn't the only thing that decides if something will dissolve — **entropy** change is important too.

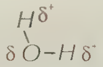
A reaction or state change is more likely when there is a positive entropy change. Dissolving normally causes an increase in entropy. But for small, highly charged ions there may be a decrease because when water molecules surround the ions, it makes things more orderly. The entropy changes are usually pretty small but they can sometimes make the difference between something being soluble or insoluble.

Learning Objectives:

- Be able to explain and use the terms enthalpy change of solution and enthalpy change of hydration.
- Be able to use the enthalpy change of solution of a simple ionic solid (e.g. NaCl, $MgCl_2$) and relevant energy terms (enthalpy change of hydration and lattice enthalpy) to construct enthalpy cycles and carry out related calculations.
- Be able to explain, in qualitative terms, the effect of ionic charge and ionic radius on the exothermic value of an enthalpy change of hydration.

Specification Reference 5.2.1

Tip: Take a look back at Module 2: Section 4 if you need a reminder about electronegativity and the δ^+ and δ^- charges on polar molecules such as water:

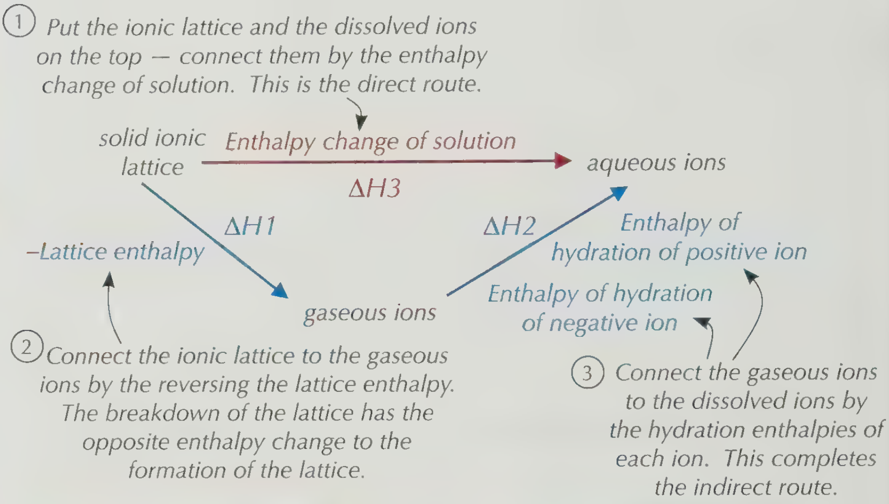


Tip: If these definitions look familiar, it's because you've seen them before on page 364.

Tip: Entropy is a measure of the disorder of a system. It's covered in loads of detail on pages 375-376 so don't worry about it too much just yet.

Calculating enthalpy change of solution

You can work out the enthalpy change of solution using an enthalpy cycle. You just need to know the lattice enthalpy of the compound and the enthalpy changes of hydration of the ions. Here's how to draw an enthalpy cycle for calculating the enthalpy change of solution:


solid ionic lattice
Enthalpy change of solution
ΔH3
aqueous ions
–Lattice enthalpy
ΔH1
ΔH2
Enthalpy of hydration of positive ion
gaseous ions
Enthalpy of hydration of negative ion

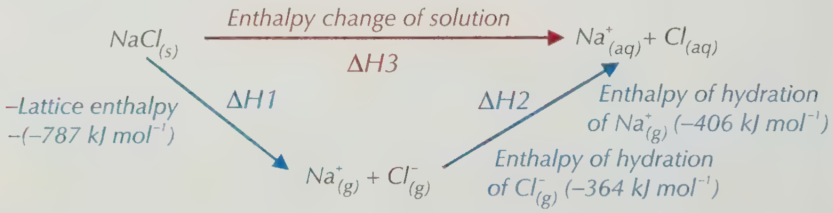
① *Put the ionic lattice and the dissolved ions on the top — connect them by the enthalpy change of solution. This is the direct route.*

② *Connect the ionic lattice to the gaseous ions by the reversing the lattice enthalpy. The breakdown of the lattice has the opposite enthalpy change to the formation of the lattice.*

③ *Connect the gaseous ions to the dissolved ions by the hydration enthalpies of each ion. This completes the indirect route.*

Example **Maths Skills**

Here's the enthalpy cycle for working out the enthalpy change of solution for sodium chloride.

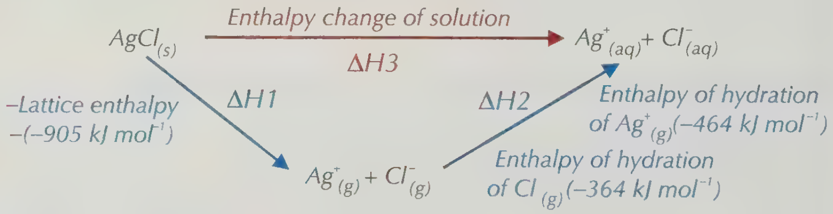

$NaCl_{(s)}$
Enthalpy change of solution
ΔH3
$Na^+_{(aq)} + Cl^-_{(aq)}$
–Lattice enthalpy
–(–787 kJ mol⁻¹)
ΔH1
ΔH2
Enthalpy of hydration of $Na^+_{(g)}$ (–406 kJ mol⁻¹)
$Na^+_{(g)} + Cl^-_{(g)}$
Enthalpy of hydration of $Cl^-_{(g)}$ (–364 kJ mol⁻¹)

From Hess's law: $\Delta_{sol}H = \Delta H3 = \Delta H1 + \Delta H2$

$= -(-787) + (-406 + -364) = \mathbf{+17\ kJ\ mol^{-1}}$

The enthalpy change of solution is slightly endothermic, but this is compensated for by a small increase in entropy, so sodium chloride still dissolves in water.

And here's another example. This enthalpy cycle is for working out the enthalpy change of solution for silver chloride.


$AgCl_{(s)}$
Enthalpy change of solution
ΔH3
$Ag^+_{(aq)} + Cl^-_{(aq)}$
–Lattice enthalpy
–(–905 kJ mol⁻¹)
ΔH1
ΔH2
Enthalpy of hydration of $Ag^+_{(g)}$ (–464 kJ mol⁻¹)
$Ag^+_{(g)} + Cl^-_{(g)}$
Enthalpy of hydration of $Cl^-_{(g)}$ (–364 kJ mol⁻¹)

From Hess's law: $\Delta_{sol}H = \Delta H3 = \Delta H1 + \Delta H2$

$= -(-905) + (-464 + -364) = \mathbf{+77\ kJ\ mol^{-1}}$

This is much more endothermic than the enthalpy change of solution for sodium chloride. There is an increase in entropy, but it's pretty small and not enough to make a difference — so silver chloride is insoluble in water.

Figure 2: *Copper(II) sulfate ($CuSO_4$) dissolved in water.*

Tip: You don't have to draw your enthalpy cycles in this triangular shape — you could use a square shape, like the Born-Haber cycles on pages 367-369.

Tip: For this enthalpy cycle, ΔH2 is equal to the two enthalpies of hydration added together.

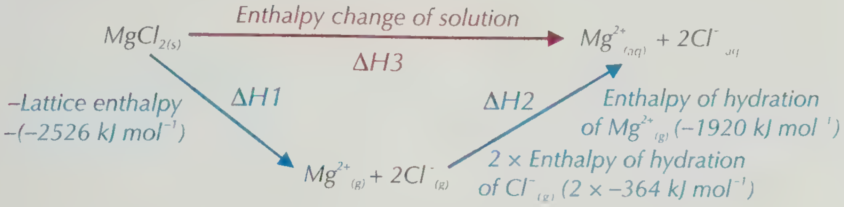
Tip: Take a look back at page 368 for more on Hess's law.

Tip: A positive enthalpy value means that a reaction is endothermic.

If 2+ or 2– ions are involved, you need to multiply the enthalpies of hydration by the number of moles of the ions that are reacting.

Example **Maths Skills**

Here's the enthalpy cycle for working out the enthalpy change of solution for magnesium chloride ($MgCl_2$).



$MgCl_{2(s)}$
Enthalpy change of solution
ΔH3
$Mg^{2+}_{(aq)} + 2Cl^-_{(aq)}$
–Lattice enthalpy
–(–2526 kJ mol⁻¹)
ΔH1
ΔH2
Enthalpy of hydration
of $Mg^{2+}_{(g)}$ (–1920 kJ mol⁻¹)
2 × Enthalpy of hydration
of $Cl^-_{(g)}$ (2 × –364 kJ mol⁻¹)
$Mg^{2+}_{(g)} + 2Cl^-_{(g)}$

In this example, there are two moles of Cl^- ions in the ionic lattice, so you have to multiply the enthalpy of hydration of Cl^- by two when you're calculating the enthalpy change of solution. So...

From Hess's law: $\Delta_{sol}H = \Delta H3 = \Delta H1 + \Delta H2$

$= -(-2526) + [-1920 + (2 \times -364)] = \mathbf{-122\ kJ\ mol^{-1}}$

$\Delta_{sol}H$ is negative, so $MgCl_2$ dissolving in water is an exothermic processes and $MgCl_2$ is soluble.

Tip: If there were three moles of an ion present in an ionic lattice you'd have to multiply the enthalpy of hydration for that ion by three to calculate the enthalpy change of solution.

Tip: If you know the enthalpy change of solution you can calculate the lattice enthalpy or an enthalpy of hydration — you just have to rearrange the equation.

Factors affecting the enthalpy of hydration

The two things that can affect the lattice enthalpy (see pages 365-366) can also affect the enthalpy of hydration. They are the charge and the size of the ions.

1. Ionic charge

Ions with a greater charge have a greater enthalpy of hydration. This is because ions with a higher charge are better at attracting water molecules than those with lower charges. More energy is released when the bonds are made, giving them a more exothermic enthalpy of hydration.

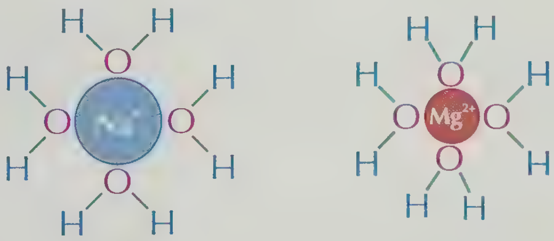
Tip: Remember — more exothermic processes have more negative enthalpy changes, more endothermic processes have more positive enthalpy changes.

2. Ionic radius

Smaller ions have a greater enthalpy of hydration. This is because smaller ions have a higher charge density than bigger ions. They attract the water molecules better and have a more exothermic enthalpy of hydration.

Example

The diagram below shows aqueous Na^+ and Mg^{2+} ions:

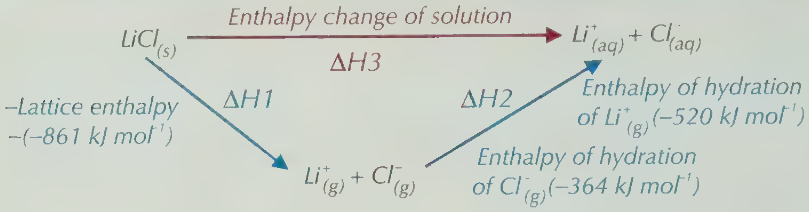


The magnesium ion is smaller and has a higher charge than the sodium ion. The higher charge and smaller size create a higher charge density. This creates a stronger attraction for the water molecules and gives it a much more negative enthalpy of hydration. The enthalpies of hydration of Mg^{2+} and Na^+ ions are: $Mg^{2+} = -1927$ kJ mol⁻¹, $Na^+ = -406$ kJ mol⁻¹

Figure 3: *Hydration of copper(II) sulfate. Because the Cu^{2+} ions are small and highly charged, this reaction is exothermic enough to produce steam.*

Practice Questions — Application

Q1 The cycle below shows the enthalpy change of solution for LiCl.


$LiCl_{(s)}$
Enthalpy change of solution
$Li^+_{(aq)} + Cl^-_{(aq)}$
ΔH3
–Lattice enthalpy
–(–861 kJ mol^{-1})
ΔH1
ΔH2
Enthalpy of hydration
of $Li^+_{(g)}$ (–520 kJ mol^{-1})
$Li^+_{(g)} + Cl^-_{(g)}$
Enthalpy of hydration
of $Cl^-_{(g)}$ (–364 kJ mol^{-1})

Calculate the enthalpy change of solution for LiCl.

Q2 a) Draw a cycle to show the enthalpy change of solution for sodium bromide. Use the following values:

Lattice enthalpy of NaBr = –747 kJ mol^{-1}
Enthalpy of hydration of Na^+ = –406 kJ mol^{-1}
Enthalpy of hydration of Br^- = –336 kJ mol^{-1}

b) Calculate the enthalpy change of solution for sodium bromide.

Q3 Use the data given in Q1 and Q2 a) and the data below to calculate enthalpy changes of solution for the following compounds:

a) lithium bromide.

b) potassium chloride.

c) magnesium bromide.

Lattice enthalpy of LiBr = –807 kJ mol^{-1}
Lattice enthalpy of KCl = –701 kJ mol^{-1}
Lattice enthalpy of $MgBr_2$ = –2440 kJ mol^{-1}
Enthalpy of hydration of K^+ = –322 kJ mol^{-1}
Enthalpy of hydration of Mg^{2+} = –1921 kJ mol^{-1}

Q4 Explain why the enthalpy of hydration of Mg^{2+} is more negative than the enthalpy of hydration of K^+.

Exam Tip
Don't be afraid to draw out an enthalpy cycle in the exam if you think it will help you answer the question.

Practice Questions — Fact Recall

Q1 a) What two processes happen when a solid ionic lattice dissolves in water?

b) State whether each of these processes is exothermic or endothermic.

Q2 The enthalpy change of solution is the combined effect of two enthalpy changes. Name them.

Q3 Give two factors which influence the enthalpy of hydration of an ion.

5. Entropy

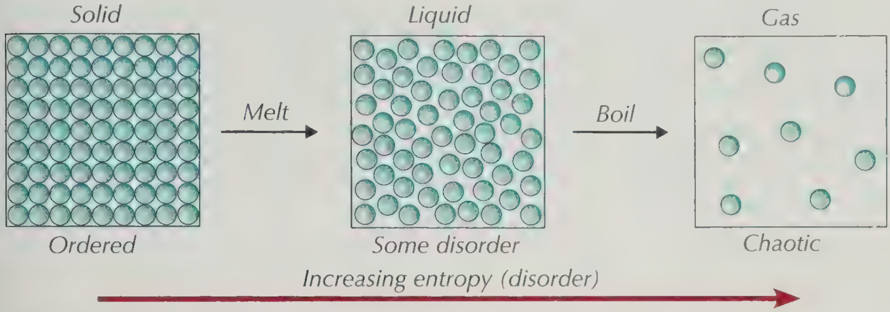
Left alone, things generally tend towards disorder — that's entropy.

What is entropy?

Entropy tells you how much disorder there is. It's a measure of the number of ways that particles can be arranged and the number of ways that the energy can be shared out between the particles — so entropy is also a measure of the dispersal of energy in a system. Substances are actually more energetically stable when there's more disorder. So the particles move to try to increase the entropy. Entropy is represented by the symbol S. There are a few things that affect entropy, such as:

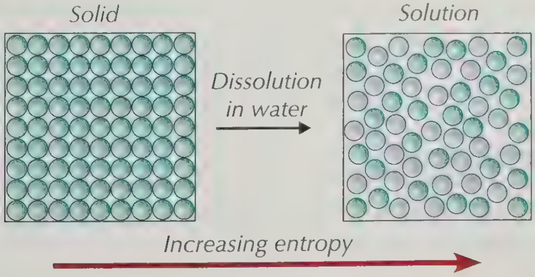
Physical state

Physical state affects entropy. You have to go back to the old 'solid-liquid-gas particle explanation thingy' to understand this. Solid particles just wobble about a fixed point — there's hardly any disorder, so they have the lowest entropy. Gas particles whizz around wherever they like. They've got the most disordered arrangements of particles, so they have the highest entropy.



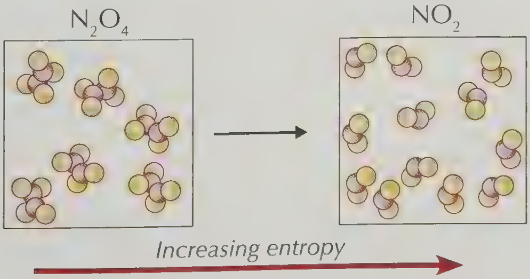
Dissolution

Dissolving a solid also increases its entropy — dissolved particles can move freely as they're no longer held in one place:



Number of gaseous particles

More gaseous particles means more entropy. It makes sense — the more gaseous particles you've got, the more ways they and their energy can be arranged. So in a reaction like $N_2O_{4(g)} \rightarrow 2NO_{2(g)}$, entropy increases because the number of gaseous moles increases:



Learning Objectives:

- Be able to explain that entropy is a measure of the dispersal of energy in a system which is greater, the more disordered a system is.
- Be able to explain the difference in magnitude of the entropy of a system:
  (i) of solids, liquids and gases,
  (ii) for a reaction in which there is a change in the number of gaseous molecules.
- Be able to calculate the entropy change of a system, ΔS, and related quantities for a reaction, given the entropies of the reactants and products.

Specification Reference 5.2.2

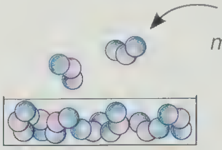
Figure 1: *Melting ice. When ice melts its entropy increases.*

Figure 2: The evaporation of water to form clouds involves an increase in entropy.

Examples

Evaporation of water

When water evaporates, there is an increase in entropy because there's a change in physical state from liquid to gas.

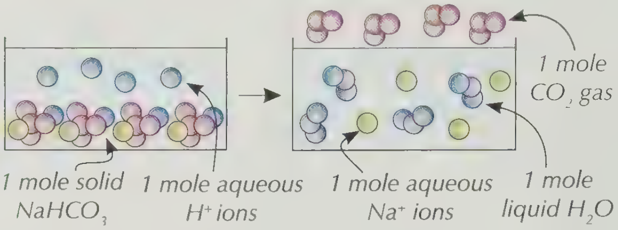


Water vapour is more chaotic than liquid water.

Reaction of $NaHCO_3$ and HCl

When sodium hydrogen carbonate reacts with hydrochloric acid there is an increase in entropy.

$$NaHCO_{3(s)} + H^+_{(aq)} \rightarrow Na^+_{(aq)} + CO_{2(g)} + H_2O_{(l)}$$



There are more particles in the products — and gases and liquids have more entropy than solids too.

Calculating entropy changes

Most reactions won't happen unless the entropy change is positive. During a reaction, there's an entropy change (ΔS) between the reactants and products.

This is just the difference between the entropies of the reactants and products.

$$\Delta S = S_{\text{products}} - S_{\text{reactants}}$$

Exam Tip
You need to be able to calculate entropy changes in your exam so make sure you learn this equation.

Example **Maths Skills**

Calculate the entropy change for the reaction of ammonia and hydrogen chloride under standard conditions.

$$NH_{3(g)} + HCl_{(g)} \rightarrow NH_4Cl_{(s)}$$

$S^\circ[NH_{3(g)}] = 192.3\ J\ K^{-1}\ mol^{-1}$
$S^\circ[HCl_{(g)}] = 186.8\ J\ K^{-1}\ mol^{-1}$
$S^\circ[NH_4Cl_{(s)}] = 94.6\ J\ K^{-1}\ mol^{-1}$

First find the entropy change of the system:

$$\Delta S = S_{\text{products}} - S_{\text{reactants}} = 94.6 - (192.3 + 186.8)$$
$$= -284.5\ J\ K^{-1}\ mol^{-1}$$

This reaction has a negative change in entropy. It's not surprising, as 2 moles of gas have combined to form 1 mole of solid.

Tip: S° is the standard entropy. The S° value of a substance is the entropy of one mole of that substance, measured under standard conditions.

Tip: When you calculate an entropy change, don't forget to give the units — they're always $J\ K^{-1}\ mol^{-1}$.

Practice Questions — Application

Q1 Solid sodium hydroxide is added to aqueous hydrogen chloride. The reaction produces sodium chloride solution. The solution is heated to produce solid sodium chloride and water vapour.

Describe the entropy changes that take place during these processes.

Q2 Using the data from Figure 3, work out the entropy change for this reaction under standard conditions:

$$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)} \quad \Delta H^\circ = -730 \text{ kJ mol}^{-1}$$

Q3 Using the data in Figure 3 work out the entropy change for this reaction under standard conditions:

$$SO_{2(g)} + 2H_2S_{(g)} \rightarrow 3S_{(s)} + 2H_2O_{(l)} \quad \Delta H^\circ = -235 \text{ kJ mol}^{-1}$$

Substance	Standard entropy of substance, S° ($J\ K^{-1}\ mol^{-1}$)
$CH_{4(g)}$	186
$O_{2(g)}$	205
$CO_{2(g)}$	214
$H_2O_{(l)}$	69.9
$SO_{2(g)}$	248
$H_2S_{(g)}$	206
$S_{(s)}$	31.6

Figure 3: *Standard entropy values for different substances.*

Practice Questions — Fact Recall

Q1 a) What is entropy?

b) Give the symbol for entropy change.

Q2 Explain how the following affect the entropy of a system:

a) a substance changing from a liquid to a gas.

b) a solid dissolving in water.

c) a reaction that results in an increased number of gaseous particles.

6. Free Energy Change

Learning Objectives:

- Be able to explain that the feasibility of a process depends upon the entropy change and temperature in the system, $T\Delta S$, and the enthalpy change of the system, ΔH.
- Be able to explain and carry out calculations of the free energy change, ΔG, as: $\Delta G = \Delta H - T\Delta S$ (the Gibbs equation) and know that a process is feasible when ΔG has a negative value.
- Be able to explain the limitations of predictions made by ΔG about feasibility, in terms of kinetics.

Specification Reference 5.2.2

Tip: The units of ΔH and ΔS must be the same. So, if you're given a value for ΔH in kJ, multiply it by 10^3 to get in J. If you want ΔG in kJ mol^{-1}, divide ΔS by 10^3 instead.

Tip: You might see free energy referred to as 'Gibbs free energy'. They're the same thing.

Figure 1: Calcium carbonate ($CaCO_3$) being heated to produce CaO and CO_2.

Everyone likes free things, so I can almost guarantee you'll like free energy.

What is free energy change?

Free energy change, ΔG, is a measure used to predict whether a reaction is **feasible**. A feasible reaction is one that, once started, will carry on to completion, without any energy being supplied to it. If ΔG is negative or equal to zero, then the reaction is feasible. Free energy change takes into account the changes in enthalpy and entropy in the system. And of course, there's a formula for it:

Free energy change (in J mol^{-1})

Entropy change (in J K^{-1} mol^{-1})

$$\Delta G = \Delta H - T\Delta S$$

Enthalpy change (in J mol^{-1})

Temperature (in K)

A negative ΔG doesn't guarantee a reaction will happen or tell you about its rate. Even if ΔG shows that a reaction is theoretically feasible, it might have a really high activation energy or be so slow that you wouldn't notice it happening at all. Here's an example of calculating free energy change.

Example **Maths Skills**

Calculate the free energy change for the following reaction at 298 K.

$$MgCO_{3(s)} \rightarrow MgO_{(s)} + CO_{2(g)} \qquad \Delta H^\circ = +117 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ = +175 \text{ J K}^{-1}\text{ mol}^{-1}$$

$$\Delta G = \Delta H - T\Delta S = +117 \times 10^3 - [298 \times (+175)]$$

$$= \mathbf{+64\ 900\ J\ mol^{-1}} \text{ (3 s.f.)}$$

ΔG is positive — so the reaction isn't feasible at this temperature.

Effect of temperature

If a reaction is exothermic (negative ΔH) and has a positive entropy change, then ΔG is always negative since $\Delta G = \Delta H - T\Delta S$. These reactions are feasible at any temperature.

If a reaction is endothermic (positive ΔH) and has a negative entropy change, then ΔG is always positive. These reactions are not feasible at any temperature. But for other combinations, temperature has an effect.

If ΔH is positive (endothermic) and ΔS is positive, then the reaction will only be feasible above a certain temperature.

Example

The decomposition of calcium carbonate is endothermic but results in an increase in entropy (the number of molecules increases and CO_2 is a gas).

$$CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}$$

The reaction only occurs when $CaCO_3$ is heated — it isn't feasible at 298 K.

If ΔH is negative (exothermic) and ΔS is negative then the reaction will only be feasible below a certain temperature.

Example

The process of turning water from a liquid to a solid is exothermic but results in a decrease in entropy (a solid is more ordered than a liquid). So it will only occur at certain temperatures (i.e. at 0 °C or below).

Here are some examples of how to decide if a reaction is feasible at different temperatures.

Examples — Maths Skills

Reaction 1: $\Delta H = +10\ \text{kJ mol}^{-1}$, $\Delta S = +10\ \text{J K}^{-1}\ \text{mol}^{-1}$

At 300 K:

$$\begin{aligned}\Delta G &= \Delta H - T\Delta S \\ &= +10 \times 10^3 - (300 \times +10) \\ &= \mathbf{+7000\ J\ mol^{-1}}\end{aligned}$$

At 1500 K:

$$\begin{aligned}\Delta G &= \Delta H - T\Delta S \\ &= +10 \times 10^3 - (1500 \times +10) \\ &= \mathbf{-5000\ J\ mol^{-1}}\end{aligned}$$

So this reaction is feasible at 1500 K, but not at 300 K.

Reaction 2: $\Delta H = -10\ \text{kJ mol}^{-1}$, $\Delta S = -10\ \text{J K}^{-1}\ \text{mol}^{-1}$

At 300 K:

$$\begin{aligned}\Delta G &= \Delta H - T\Delta S \\ &= -10 \times 10^3 - (300 \times -10) \\ &= \mathbf{-7000\ J\ mol^{-1}}\end{aligned}$$

At 1500 K:

$$\begin{aligned}\Delta G &= \Delta H - T\Delta S \\ &= -10 \times 10^3 - (1500 \times -10) \\ &= \mathbf{+5000\ J\ mol^{-1}}\end{aligned}$$

So this reaction is feasible at 300 K, but not at 1500 K.

Tip: Don't forget — the value of ΔG has to be less than or equal to zero for a reaction to be feasible.

When ΔG is zero, a reaction is just feasible. You can find the temperature when ΔG is zero by rearranging the free energy equation.

$\Delta G = \Delta H - T\Delta S$, so when $\Delta G = 0$, $T\Delta S = \Delta H$. So:

temperature at which a reaction becomes feasible (in K)

$$T = \frac{\Delta H}{\Delta S}$$

enthalpy change (in J mol⁻¹)

entropy change (in J K⁻¹ mol⁻¹)

Substance	Standard entropy of substance, S° ($\text{J K}^{-1}\ \text{mol}^{-1}$)
$WO_{3(s)}$	76.0
$H_{2(g)}$	65.0
$W_{(s)}$	33.0
$H_2O_{(g)}$	189.0

Figure 2: *Standard entropy values for different substances.*

Tip: For more on the ΔS formula, see page 376.

Example — Maths Skills

Tungsten, W, can be extracted from its ore, WO_3, by reduction using hydrogen.

$$WO_{3(s)} + 3H_{2(g)} \rightarrow W_{(s)} + 3H_2O_{(g)} \qquad \Delta H^\circ = +117\ \text{kJ mol}^{-1}$$

Use the data in Figure 2 to find the minimum temperature at which the reaction becomes feasible.

First, convert the enthalpy change, ΔH, to joules per mole:

$$\Delta H = 117 \times 10^3\ \text{J mol}^{-1} = 117\ 000\ \text{J mol}^{-1}$$

Then find the entropy change, ΔS:

$$\begin{aligned}\Delta S = S_{\text{products}} - S_{\text{reactants}} &= [33.0 + (3 \times 189.0)] - [76.0 + (3 \times 65.0)] \\ &= +329\ \text{J K}^{-1}\ \text{mol}^{-1}\end{aligned}$$

Then divide ΔH by ΔS to find the temperature at which the reaction just becomes feasible:

$$T = \frac{\Delta H}{\Delta S} = \frac{117\ 000}{329} = \mathbf{356\ K}$$

Substance	Standard entropy of substance, S° ($J\ K^{-1}\ mol^{-1}$)
$Al_2O_{3(s)}$	51.0
$Mg_{(s)}$	32.5
$Al_{(s)}$	28.3
$MgO_{(s)}$	27.0

Figure 3: *Standard entropy values for different substances.*

Tip: When calculating free energy changes, be really careful with your units. The temperature must be in K (add 273 if it's given in °C) and the enthalpy and entropy values should involve J not kJ.

Practice Questions — Application

Q1 Using the data from Figure 3 for this reaction under standard conditions: $Al_2O_{3(s)} + 3Mg_{(s)} \rightarrow 2Al_{(s)} + 3MgO_{(s)}$ $\Delta H^\circ = -130\ kJ\ mol^{-1}$

a) calculate ΔS.

b) calculate ΔG.

c) explain whether the reaction is feasible at 298 K.

Q2 Consider the reaction below:

$$ZnCO_{3(s)} \rightarrow ZnO_{(s)} + CO_{2(g)}$$

$$\Delta H^\circ = +71.0\ kJ\ mol^{-1} \qquad \Delta S = +176\ J\ K^{-1}\ mol^{-1}$$

a) Determine whether or not this reaction is feasible at:

(i) 298 K (ii) 600 K

b) Calculate the temperature at which this reaction becomes feasible.

Q3 Calculate the temperature at which this reaction becomes feasible:

$$CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}$$

$$\Delta H^\circ = +178\ kJ\ mol^{-1} \qquad \Delta S = +165\ J\ K^{-1}\ mol^{-1}$$

Practice Questions — Fact Recall

Q1 a) What is free energy change?

b) Give the symbol for free energy change.

Q2 Give the formula needed to work out free energy change.

Q3 Suggest two reasons why a reaction might not happen, even if it has a negative free energy change value.

Q4 A reaction is endothermic, has a negative entropy change and so has a positive value for free energy. Is this reaction feasible?

Q5 Give the formula that you'd use to calculate the temperature at which a reaction becomes feasible.

Section Summary

Make sure you know...

- That enthalpy change is the heat energy transferred in a reaction at constant pressure, and the symbol for it is ΔH.
- That exothermic reactions have negative ΔH values and endothermic reactions have positive ΔH values.
- The definitions of enthalpy change of formation, enthalpy change of atomisation for elements and for compounds, ionisation energy, and electron affinity.
- The definition of the lattice enthalpy, $\Delta_{LE}H$.
- How lattice enthalpy is affected by ionic charge and ionic radius.
- How to construct Born-Haber cycles and use them to calculate lattice enthalpies and related values.
- The definitions of enthalpy change of hydration, $\Delta_{hyd}H$, and enthalpy change of solution, $\Delta_{sol}H$.
- The different enthalpy changes that take place when a solid ionic lattice dissolves.
- How to use enthalpy cycles to calculate enthalpies of solution and related values.
- How enthalpy of hydration is influenced by ionic charge and ionic radius.
- That entropy, S, is a measure of the dispersal of energy in a system and that a system becomes energetically more stable when it becomes more disordered.
- How entropy is affected by physical state and number of particles.
- How to calculate the entropy change, and related values, for a reaction.
- That the tendency of a reaction to happen depends on temperature, entropy and enthalpy.
- That it's the balance between entropy and enthalpy that determines the feasibility of a reaction.
- What free energy change is and how to calculate it using $\Delta G = \Delta H - T\Delta S$.
- That the feasibility of some reactions depends on temperature, and how to calculate the temperature at which a reaction becomes feasible.
- That feasibility predictions, based on the free energy change value, are limited because reactions may have a very high activation energy or very slow rate of reaction.

Exam-style Questions

1 Which of the following ionic compounds would you expect to have the most negative standard lattice enthalpy?

A BeO

B NaCl

C KBr

D MgS

(1 mark)

2 The following reaction is feasible at any temperature:

$$H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(g)}$$

Which statement about this reaction is true?

A The enthalpy change is positive and the entropy change is positive.

B The enthalpy change is positive and the entropy change is negative.

C The enthalpy change is negative and the entropy change is positive.

D The enthalpy change is negative and the entropy change is negative.

(1 mark)

3 Strontium fluoride is a solid ionic lattice which dissolves in water and can be used as an optical coating for lenses.

(a) Draw an enthalpy cycle for the enthalpy change of solution of $SrF_{2(s)}$. Label each enthalpy change.

(2 marks)

(b) Calculate the enthalpy change of solution for SrF_2, using the data in the table below.

(2 marks)

Enthalpy change	**ΔH° / kJ mol^{-1}**
Lattice enthalpy of $SrF_{2(s)}$	–2492
Enthalpy change of hydration of Sr^{2+} ions	–1480
Enthalpy change of hydration of F^- ions	–506

4 Manganese can be extracted from its ore manganese(IV) oxide, MnO_2, by reduction using carbon at 1473 K. The reaction is shown in the equation below.

$$MnO_{2\,(s)} + C_{(s)} \rightarrow Mn_{(s)} + CO_{2\,(g)} \qquad \Delta H^{\circ} = +127\ \text{kJ mol}^{-1}$$

	$MnO_{2\,(s)}$	$C_{(s)}$	$Mn_{(s)}$	$CO_{2\,(g)}$
S°/ J $K^{-1}mol^{-1}$	53.0	5.70	32.0	214

(a) Use the balanced equation to explain whether you would expect entropy to decrease or increase during this reaction.

(1 mark)

(b) Calculate the free energy change for the extraction of manganese from its ore.

(4 marks)

(c) Explain how the free energy change of a reaction relates to the feasibility of that reaction.

(1 mark)

(d) Give the equation which links the temperature at which a reaction becomes feasible, T, the enthalpy change for the reaction, ΔH, and the entropy change, ΔS.

(1 mark)

(e) Calculate the temperature at which the reduction of manganese oxide using carbon becomes feasible.

(2 marks)

The standard enthalpy of change formation of MnO_2 is –521 kJ mol^{-1}.

(f) Define the term enthalpy change of formation.

(1 mark)

(g) State whether the formation of manganese(IV) oxide from manganese and oxygen will be endothermic or exothermic.

(1 mark)

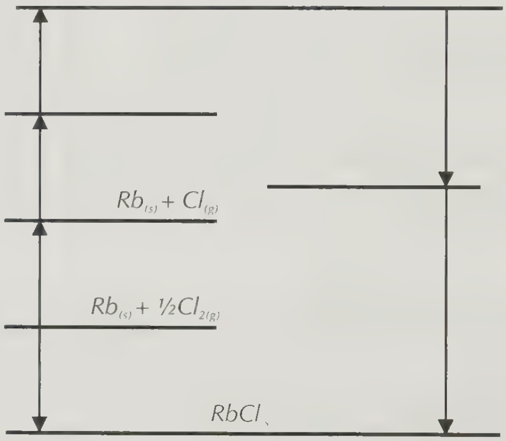
5 Rubidium chloride is an ionic compound that dissolves easily in water and can be used as a cell marker in laboratories. The table below shows thermodynamic data for rubidium chloride.

Enthalpy change	**ΔH° / kJ mol^{-1}**
Enthalpy change of atomisation of rubidium	+81
First ionisation enthalpy of rubidium	+403
Enthalpy change of hydration of Rb^+ ions	–296
Enthalpy change of atomisation of chlorine	+122
Electron affinity of chlorine	–349
Enthalpy change of hydration of Cl^- ions	–364
Enthalpy change of formation of rubidium chloride	–435

(a) Define the term lattice enthalpy.

(1 mark)

(b) Complete the Born-Haber cycle for the formation of rubidium chloride by filling in the blank lines. You should include chemical symbols and state symbols.



(3 marks)

(c) Use the data in the table to calculate the standard lattice enthalpy of rubidium chloride.

(3 marks)

(d) The standard lattice enthalpy of sodium chloride is more exothermic than that of rubidium chloride. Explain why.

(3 marks)

(e) Calculate the enthalpy change of solution for rubidium chloride.
(If you have not been able to answer **(c)** use the value of –300 kJ mol^{-1} for the standard lattice enthalpy of rubidium chloride. This value is incorrect.)

(2 marks)

1. Redox Reactions

You've already done a bit about redox reactions in the first year of the course. Here's a reminder, plus a bit more about writing equations for redox reactions.

Learning Objectives:

- Be able to explain and use the terms *oxidising agent* and *reducing agent*.
- Be able to construct redox equations using half-equations and oxidation numbers.
- Be able to interpret and predict reactions involving electron transfer.

Specification Reference 5.2.3

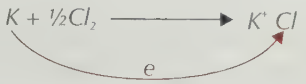
What is a redox reaction?

A loss of electrons is called **oxidation**. A gain of electrons is called **reduction**. Reduction and oxidation happen simultaneously — hence the term 'redox' reaction. An **oxidising agent** accepts electrons and gets reduced. A **reducing agent** donates electrons and gets oxidised.

Example

In the reaction between potassium and chlorine:

Potassium is the reducing agent — it donates electrons and gets oxidised.



Chlorine is the oxidising agent — it accepts electrons and gets reduced.

Half-equations

A redox reaction is made up of an oxidation half-reaction and a reduction half-reaction. You can write an ionic **half-equation** for each half-reaction.

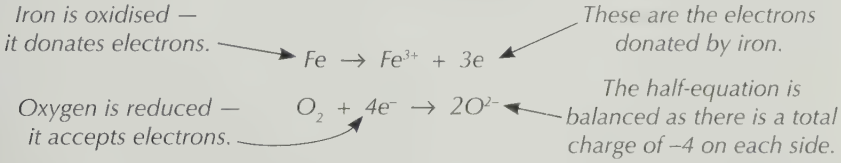

Iron is oxidised — it donates electrons.
$Fe \rightarrow Fe^{3+} + 3e$
These are the electrons donated by iron.
Oxygen is reduced — it accepts electrons.
$O_2 + 4e^- \rightarrow 2O^{2-}$
The half-equation is balanced as there is a total charge of –4 on each side.

Figure 1: *Half-equations for the oxidation of iron and the reduction of oxygen.*

An oxidation half-equation can be combined with a reduction half-equation to make a full redox equation.

Example **Maths Skills**

Zinc metal displaces silver ions from silver nitrate solution to form a solution of zinc ions and a deposit of silver metal.

The zinc atoms each lose 2 electrons (oxidation): $Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$

The silver ions each gain 1 electron (reduction): $Ag^+_{(aq)} + e^- \rightarrow Ag_{(s)}$

Two silver ions are needed to accept the two electrons released by each zinc atom. So you need to double the silver half-equation before the two half-equations can be combined:

$$2Ag^+_{(aq)} + 2e^- \rightarrow 2Ag_{(s)}$$

Now the number of electrons lost and gained balance, so the half-equations can be combined:

$$Zn_{(s)} + 2Ag^+_{(aq)} + 2e^- \rightarrow Zn^{2+}_{(aq)} + 2e^- + 2Ag_{(s)}$$

The electrons cancel each other out, so this is the overall redox equation:

$$Zn_{(s)} + 2Ag^+_{(aq)} \rightarrow Zn^{2+}_{(aq)} + 2Ag_{(s)}$$

Tip: Don't forget:
OIL RIG
Oxidation Is Loss
Reduction Is Gain
(...of electrons)

Tip: Electrons are shown in half-equations so that the charges balance.

Tip: It's a good idea to check that the charges balance in your final redox equation. If they don't, you've probably done something wrong somewhere...

Tip: If you see Roman numerals in a chemical name, it's an oxidation number (see below). For example, in dichromate(VI) ions, chromium has an oxidation number of +6.

Balancing more complex half-equations

Sometimes you might have to write a half-equation for a more complicated reaction where the oxidising or reducing agent contains oxygen or hydrogen (for example dichromate(VI) ions, $Cr_2O_7^{2-}$). In this case you might have to add water and either H^+ or OH^- ions to make the half-equations balance.

You can always add electrons and water (H_2O) to your half-equations to balance them. If the reaction is taking place under acidic conditions, then you can also add H^+ ions. If the reaction is taking place under alkaline conditions, then you can add OH^- ions to balance your half-equation. But that's it — those are the only things that you're allowed to add.

Tip: 'Acidified' just means that some acid has been added to the oxidising agent. It's telling you that the reaction is taking place under acidic conditions.

Example — **Maths Skills**

As part of a redox reaction, acidified dichromate(VI) ions, $Cr_2O_7^{2-}$, are reduced to Cr^{3+} ions. Write a half-equation for this reaction.

Start by balancing all the elements in the reaction except for O and H. Here, this just means balancing the number of Cr atoms in the dichromate(VI) ions on the left-hand side of the reaction and the Cr^{3+} ions on the right-hand side:

$$Cr_2O_7^{2-} \rightarrow 2Cr^{3+}$$

Now balance the oxygen atoms. Since the reaction is taking place under acidic conditions there won't be any OH^- ions around. So you add seven H_2O molecules to the right-hand side to balance the oxygen in $Cr_2O_7^{2-}$:

$$Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 7H_2O$$

Then balance the hydrogen atoms from the water by adding some H^+ ions (from the acid) to the left-hand side:

$$Cr_2O_7^{2-} + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O$$

Tip: You could also balance this reaction by looking at the changes in oxidation numbers (see next page).

Finally, add some electrons to balance the charges:

$$\begin{array}{lccccccc} & Cr_2O_7^{2-} & + 14H^+ & + 6e^- & \rightarrow & 2Cr^{3+} & + & 7H_2O \\ \textit{Charges:} & (-2) & (+1\times14) & (-6) & \rightarrow & (+3\times2) & & (0\times7) \\ \textit{Total:} & & +6 & & \rightarrow & & +6 & \end{array}$$

Oxidation numbers

Tip: You might see oxidation numbers called oxidation states. They're the same thing though.

The **oxidation number** of an element tells you the total number of electrons it has donated or accepted. Oxidation numbers go up or down as electrons are lost or gained. To work out which atoms are oxidised and which are reduced in a reaction, you need to look at the oxidation numbers.
The oxidation number for an atom will increase by one for each electron lost.
The oxidation number will decrease by one for each electron gained.

Tip: Look back at pages 95-96 for the rules on how to assign oxidation numbers.

Example

The reaction between vanadium(V) oxide and sulfur dioxide is shown below:

$$\begin{array}{lccccccl} & V_2O_5 & + & SO_2 & \rightarrow & V_2O_4 & + & SO_3 \\ \textit{Oxidation number of V:} & +5 & & & \rightarrow & +4 & & \textit{reduction} \\ \textit{Oxidation number of S:} & & & +4 & \rightarrow & & +6 & \textit{oxidation} \end{array}$$

In this reaction, vanadium is reduced from +5 to +4 (it gains 1 electron) and sulfur is oxidised from +4 to +6 (it loses two electrons).

You can also use changes in oxidation numbers to write redox equations.

Example — Maths Skills

Acidified manganate(VII) ions (MnO_4^-) can be reduced to manganese(II) ions by iron(II) ions. The iron(II) ions are oxidised to iron(III) ions. Write an overall redox equation for this reaction.

1. In the question you're told that iron changes from iron(II) to iron(III) — its oxidation number has increased by 1, so it must have lost one electron:

$$Fe^{2+} \rightarrow Fe^{3+} + e^-$$

2. You're also told that manganate(VII) is reduced to manganese(II) — its oxidation number has decreased by 5, so it must have gained 5 electrons:

$$MnO_4^- + 5e^- \rightarrow Mn^{2+}$$

But this half-equation isn't balanced — you need to add some water to the right-hand side and then some hydrogen ions to the left-hand side:

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$

3. Five iron ions are required to release the five electrons needed by each manganate ion, so you need to multiply the first half-equation by 5:

$$5Fe^{2+} \rightarrow 5Fe^{3+} + 5e^-$$

4. Now you can combine the half-equations:

$$MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$$

Tip: Remember to finish by checking that the charges balance — that way you know you haven't made a mistake.

Practice Questions — Application

Q1 Metallic iron can displace copper(II) ions in solution to form a solution of iron(III) ions and a deposit of copper metal. The half-equations are:

$$Fe_{(s)} \rightarrow Fe^{3+}_{(aq)} + 3e^- \qquad Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$$

Combine these half-equations to give the full redox equation for this reaction.

Q2 The following reaction occurs between iron and chlorine:

$$Cl_{2(g)} + 2Fe^{2+}_{(aq)} \rightarrow 2Cl^-_{(aq)} + 2Fe^{3+}_{(aq)}$$

One of the half-equations is $Fe^{2+}_{(aq)} \rightarrow Fe^{3+}_{(aq)} + e^-$. Write out the other.

Q3 Dichromate ions ($Cr_2O_7^{2-}$) are reduced by zinc. The unbalanced half-equations for this reaction are:

$$Zn \rightarrow Zn^{2+} + e^- \quad \text{and} \quad Cr_2O_7^{2-} + H^+ + e^- \rightarrow Cr^{3+} + H_2O$$

a) Balance both of these half-equations

b) Give the full redox equation for this reaction.

Q4 Ethanol, CH_3CH_2OH, can be oxidised to ethanoic acid, CH_3COOH, using an acidified solution of dichromate(VI) ions, $Cr_2O_7^{2-}{}_{(aq)}$.

a) What is the oxidation state of chromium in dichromate(VI) ions?

b) Write out half-equations for the oxidation and reduction reactions.

c) Write a balanced redox equation for this reaction.

Tip: Writing the half-equation for the oxidation of ethanol in Q4 is a bit tricky, but don't panic — just use the method from the last page. First check that the carbons are balanced. Then add some water to balance the oxygens. Then add some H^+ ions to balance the hydrogens. Finally, balance the charges by adding some electrons.

Tip: The oxidation of alcohols by dichromate(VI) ions can be used as a test for primary or secondary alcohols. It's all covered on pages 251-252.

Practice Questions — Fact Recall

Q1 a) What is an oxidising agent?

b) What is a reducing agent?

Q2 What happens to the oxidation number of an element that is reduced as part of a redox reaction?

2. Redox Titrations

Learning Objectives:

- Know the techniques and procedures used when carrying out redox titrations including those involving Fe^{2+}/MnO_4^-.
- Be able to perform structured and non-structured titration calculations, based on experimental results of redox titrations involving Fe^{2+}/MnO_4 and non-familiar redox systems.

Specification Reference 5.2.3

You learnt all about redox reactions on pages 385-387 (and if you haven't, you should). Now here's a nice topic all about how you can use redox reactions in experimental chemistry.

Oxidising and reducing agents

Transition (d-block) elements can exist in many different **oxidation numbers** (see page 416). They can change oxidation number by gaining or losing electrons in redox reactions (see pages 428-429). The ability to gain or lose electrons easily makes transition metal ions good oxidising or reducing agents. What's more, as they change oxidation number, transition elements often also change colour, so it's easy to spot when they've been oxidised or reduced. Here are a couple of examples:

Examples

The oxidation of Fe^{2+} to Fe^{3+} by manganate(VII) ions in solution.

Acidified potassium manganate(VII) solution, $KMnO_{4(aq)}$, is used as an oxidising agent. It contains manganate(VII) ions (MnO_4^-), in which manganese has an oxidation number of +7. They can be reduced to Mn^{2+} ions during a redox reaction with Fe^{2+} ions.

Half equations:

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$

$$5Fe^{2+} \rightarrow 5Fe^{3+} + 5e^-$$

$$MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$$

In this reaction the manganese is reduced and the iron is oxidised. $MnO_4^-{}_{(aq)}$ is purple and $[Mn(H_2O)_6]^{2+}{}_{(aq)}$ is such a pale pink that it looks colourless, so during this reaction you'll see a colour change from purple to colourless — see Figure 1.

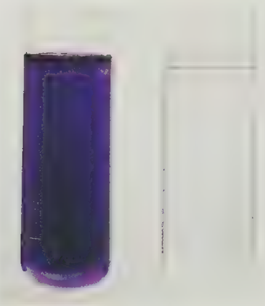


Figure 1: The colour change seen during the reaction of potassium manganate(VII) solution with iron(II) ions. The solution goes from purple to colourless as the manganate(VII) ions are reduced to Mn^{2+} ions.

The oxidation of Zn to Zn^{2+} by dichromate(VI) ions in solution.

Acidified potassium dichromate(VI) solution, $K_2Cr_2O_{7(aq)}$, is another oxidising agent. It contains dichromate(VI) ions ($Cr_2O_7^{2-}$), in which chromium has an oxidation number of +6. They can be reduced to Cr^{3+} ions during a redox reaction with Zn metal.

Half equations:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$

$$3Zn \rightarrow 3Zn^{2+} + 6e^-$$

$$Cr_2O_7^{2-} + 14H^+ + 3Zn \rightarrow 2Cr^{3+} + 7H_2O + 3Zn^{2+}$$

In this reaction the chromium is reduced and the zinc is oxidised. $Cr_2O_7^{2-}{}_{(aq)}$ is orange and $[Cr(H_2O)_6]^{3+}{}_{(aq)}$ looks green so, during this reaction, you'll see a colour change from orange to green — see Figure 2.

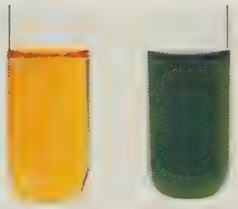


Figure 2: The colour change seen during the reaction of potassium dichromate(VI) solution with zinc. The solution goes from orange to green as the dichromate(VI) ions are reduced to Cr^{3+} ions.

The pretty colours of transition metal ion solutions make them really useful as indicators. The sharp colour changes let you know when a reaction has taken place. This characteristic of transition metal ions is especially useful in titrations, as you'll see on the next few pages...

Performing titrations

Titrations using transition element ions let you find out how much oxidising agent is needed to exactly react with a quantity of reducing agent — they're **redox titrations**. If you know the concentration of either the oxidising agent or the reducing agent, you can use the titration results to work out the concentration of the other. Here's how.

- First, measure out a quantity of reducing agent, e.g. aqueous Fe^{2+} ions, using a pipette, and put it in a conical flask.
- Use a measuring cylinder to measure out about 20 cm^3 of dilute sulfuric acid and add it to the flask — this is in excess, so you don't have to be too exact. (The acid is added to make sure there are plenty of H^+ ions to allow the oxidising agent to be reduced.)
- Add some oxidising agent (e.g. potassium manganate(VII) solution) to a burette and take a reading of the initial volume.
- Now gradually add the oxidising agent to the reducing agent. Swirl the flask as you go.
- The oxidising agent you are adding will react with the reducing agent. This reaction will continue until all of the reducing agent is used up.
- At this point, the very next drop that you add will give the mixture the colour of the oxidising agent.
- Stop when the mixture in the flask becomes just tainted with the colour of the oxidising agent (the end point) and note down the volume of oxidising agent that you added. This is the rough titration.
- Now do some accurate titrations. Measure out the solutions and take an initial reading. Run the oxidising agent into the reducing agent until you are within 2 cm^3 of the end point from your rough titration. Then add the oxidising agent drop by drop until you reach the exact end point.
- Record the final volume of oxidising agent in the burette. Subtract this from the initial reading to find the exact volume of oxidising agent needed to react with the reducing agent — this is called the titre.
- Repeat until you get at least three readings within 0.10 cm^3 of each other.

The equipment you'll need to do a titration is shown in Figure 3.

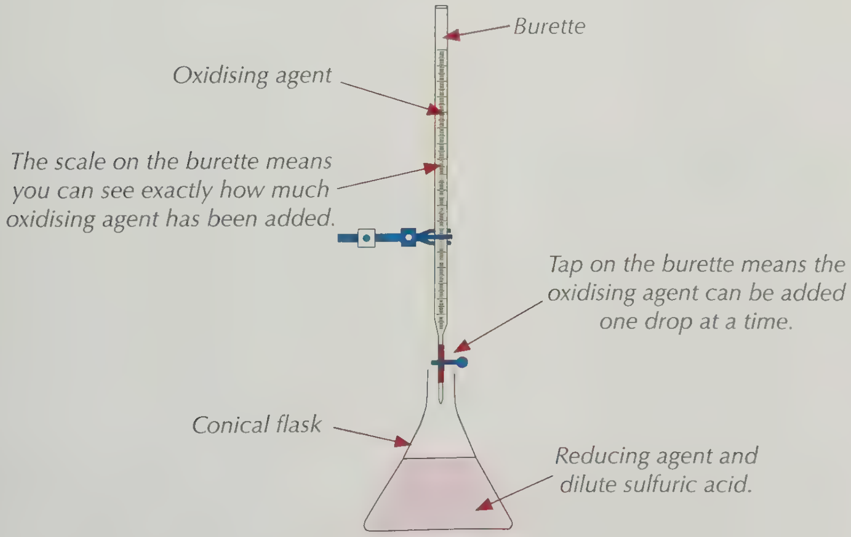

Burette
Oxidising agent
The scale on the burette means you can see exactly how much oxidising agent has been added.
Tap on the burette means the oxidising agent can be added one drop at a time.
Conical flask
Reducing agent and dilute sulfuric acid.

Figure 3: *The equipment needed to perform a redox titration.*

Tip: Before carrying out any experiment, do a full risk assessment and take any necessary safety precautions.

Tip: You've already seen how to do acid-base titrations and accurately measure out volumes of liquids on pages 83-84. Have a look back if you could do with a refresher.

Tip: You can also do titrations the other way round — adding the reducing agent to the oxidising agent.

Tip: You could use a coloured reducing agent and a colourless oxidising agent instead — then you'd be watching for the moment that the colour in the flask disappears.

Tip: Readings that are within a small range are known as concordant results.

Tip: Remember to read any volume measurements from the bottom of the meniscus, and at eye-level.

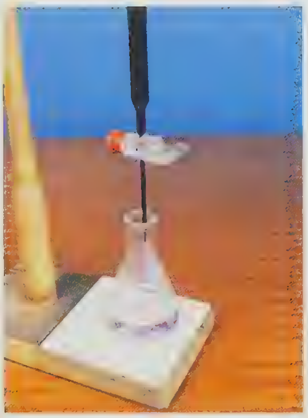


***Figure 4:** $KMnO_4$ being added to Fe^{2+} ions. The solution in the flask is just tinted purple, so the titration is at the end point.*

Titrations using $KMnO_4$

Manganate(VII) ions (MnO_4^-) in aqueous potassium manganate(VII) ($KMnO_4$) are purple. When they're added to the reducing agent, they start reacting. This reaction will continue until all of the reducing agent is used up. At this point the solution in the flask will start to turn purple. The exact point at which the solution turns from colourless to purple is the end point of the reaction. The trick is to spot exactly when this happens. Doing the reaction in front of a white surface (for example, by putting the flask on a white tile, as in Figure 4) can make the colour change much easier to spot.

Calculating the concentration of a reagent

Once you've done a titration you can use your results to calculate the concentration of either the oxidising agent or the reducing agent. To do this:

Step 1: Write out a balanced equation for the redox reaction that's happening in the conical flask.

Step 2: Decide what you know already and what you need to know — usually you'll know the two volumes and the concentration of one of the reagents and want to find the concentration of the other reagent.

Tip: These calculations are the same as the ones for acid-base titrations (see pages 87-89).

Step 3: For the reagent you know both the concentration and the volume of, calculate the number of moles present using the equation:

$$\text{moles} = \frac{\text{concentration (mol dm}^{-3}) \times \text{volume (cm}^3)}{1000}$$

Step 4: Use the molar ratios in the balanced equation to find out how many moles of the other reagent were present in the solution.

Tip: The molar ratio is the ratio of one ion (or compound) to another ion (or compound) in the balanced equation.

Step 5: Calculate the unknown concentration using the equation:

$$\text{concentration (mol dm}^{-3}) = \frac{\text{moles} \times 1000}{\text{volume (cm}^3)}$$

Example — **Maths Skills**

27.5 cm^3 of 0.0200 mol dm^{-3} aqueous potassium manganate(VII) reacted with 25.0 cm^3 of acidified iron(II) sulfate solution.
Calculate the concentration of Fe^{2+} ions in the solution.

1. The balanced equation for this titration reaction is:

$$MnO_4^-{}_{(aq)} + 8H^+_{(aq)} + 5Fe^{2+}_{(aq)} \rightarrow Mn^{2+}_{(aq)} + 4H_2O_{(l)} + 5Fe^{3+}_{(aq)}$$

2. You know the concentration and the volume of the MnO_4^- ion solution (0.0200 mol dm^{-3} and 27.5 cm^3) and the volume of the Fe^{2+} solution (25.0 cm^3). You need to know the concentration of the Fe^{2+} solution.

3. Work out the number of moles of MnO_4^- ions added to the flask.

$$\text{moles } MnO_4^- = \frac{\text{conc.} \times \text{volume}}{1000} = \frac{0.0200 \times 27.5}{1000} = 5.50 \times 10^{-4} \text{ moles}$$

4. From the molar ratios in the equation, you know 1 mole of MnO_4^- reacts with 5 moles of Fe^{2+}. So 5.50×10^{-4} moles of MnO_4^- must react with $(5.50 \times 10^{-4}) \times 5 = 2.75 \times 10^{-3}$ moles of Fe^{2+}.

5. Calculate the concentration of Fe^{2+}:

$$\text{conc. } Fe^{2+} = \frac{\text{moles} \times 1000}{\text{volume}} = \frac{(2.75 \times 10^{-3}) \times 1000}{25.0} = \mathbf{0.110 \text{ mol dm}^{-3}}$$

Exam Tip
In your exams, you could be asked to carry out titration calculations using chemicals and systems you've not met before. If this happens, don't panic. Just follow the method above and you should be fine.

Tip: In these calculations the units of concentration should always be mol dm^{-3}.

Practice Questions — Application

Q1 28.2 cm^3 of a 0.0500 mol dm^{-3} acidified iron(II) sulfate solution reacted exactly with 30.0 cm^3 of aqueous potassium manganate(VII).

a) Write an ionic equation for the reaction between Fe^{2+} ions and MnO_4^- ions.

b) Calculate the number of moles of acidified iron(II) sulfate solution that reacted with the aqueous potassium manganate(VII).

c) Use your answer from part b) to calculate the concentration of the potassium manganate(VII) solution.

Q2 Aqueous potassium manganate(VII) with a concentration of 0.0750 mol dm^{-3} was used to completely react with 28.0 cm^3 of a 0.600 mol dm^{-3} solution of acidified iron(II) sulfate. Calculate the volume of potassium manganate(VII) solution that reacted.

Q3 22.2 cm^3 of 0.150 mol dm^{-3} aqueous potassium dichromate(VI) was needed to completely react with 20.0 cm^3 of an acidified iron(II) sulfate solution.

a) Write down the balanced ionic equation for the reaction between Fe^{2+} ions and $Cr_2O_7^{2-}$ ions.

b) Calculate the number of moles of aqueous potassium dichromate(VI) that reacted with the acidified iron(II) sulfate solution.

c) Calculate the concentration of Fe^{2+} ions in the solution.

Q4 A 0.450 mol dm^{-3} solution of acidified iron(II) sulfate completely reacted with 24.0 cm^3 of a 0.0550 mol dm^{-3} solution of aqueous potassium dichromate(VI). Calculate the volume of iron(II) sulfate solution used.

Q5 A lump of zinc metal was dropped into 30.0 cm^3 of a 0.230 mol dm^{-3} solution of acidified dichromate(VI) ions.

a) Write a balanced ionic equation for this reaction.

b) Calculate the number of moles of dichromate(VI) ions present in the solution.

c) The lump of zinc fully dissolved in the solution. Calculate the mass of zinc that was added to the solution. Assume that all of the acidified dichromate(VI) solution reacted. (You will need to use the equation mass = moles × M_r).

Exam Tip
These questions are quite wordy. In the exams, you might find it helpful to underline the key bits of information in the question.

Tip: It may help to swot up on your acid-base titration calculations before you start these — they're all covered on pages 87-89.

Tip: Question 5 is a bit different because there's a solid and a solution involved. But you still start your calculations by following the same steps.

Practice Questions — Fact Recall

Q1 Give an example of an oxidising agent.

Q2 Why is acid added to the reducing agent in redox titrations?

Q3 How do you know when you've reached the end point of a titration?

Learning Objectives:

- Know the techniques and procedures used when carrying out redox titrations including those involving $I_2/S_2O_3^{2-}$.
- Be able to perform structured and non-structured titration calculations, based on experimental results of redox titrations involving $I_2/S_2O_3^{2-}$ and non-familiar redox systems.

Specification Reference 5.2.3

Tip: Make sure you carry out a risk assessment before starting any experiment.

Exam Tip
If you have to write out these equations in the exams, make sure they're balanced. You'll lose easy marks if they're not.

3. More on Titrations

More titrations... hurrah. As well as knowing all about acid-base titrations (which came up in Module 2: Section 3) and Fe^{2+}/MnO_4^- titrations (pages 388-390), you also need to know about iodine-sodium thiosulfate titrations. Keep learning...

Iodine-sodium thiosulfate titrations

Iodine-sodium thiosulfate titrations are a way of finding the amount of iodine in a solution. If the iodine has been formed in a redox reaction, knowing the amount of iodine allows you to work out the amount of other substances involved in the reaction too — for example, the amount of oxidising agent present. So here's how you can find out the concentration of a solution of the oxidising agent potassium iodate(V):

Step 1: Oxidise the iodide ions to iodine

Measure out a certain volume of potassium iodate(V) solution (KIO_3) (the oxidising agent) — say 25 cm³. Add this to an excess of acidified potassium iodide solution (KI). The iodate(V) ions in the potassium iodate(V) solution oxidise some of the iodide ions to iodine — the solution will be red-brown.

$$IO_3^-{}_{(aq)} + 5I^-{}_{(aq)} + 6H^+{}_{(aq)} \rightarrow 3I_{2\,(aq)} + 3H_2O_{(l)}$$

Step 2: Titrate the iodine solution with sodium thiosulfate

You need to titrate the solution formed in step 1 with sodium thiosulfate ($Na_2S_2O_3$) of a known concentration. The iodine in the solution reacts with thiosulfate ions like this:

$$I_{2\,(aq)} + 2S_2O_3^{2-}{}_{(aq)} \rightarrow 2I^-{}_{(aq)} + S_4O_6^{2-}{}_{(aq)}$$

The set-up for this titration is shown in Figure 1. Here's how you carry it out:

- Take the flask containing the solution that was produced in Stage 1.
- From a burette, add sodium thiosulfate solution to the flask drop by drop.
- It's hard to see the end point, so when the iodine colour fades to a pale yellow, add 2 cm³ of starch solution (to detect the presence of iodine). The solution in the conical flask will go dark blue, showing there's still some iodine there.
- Add sodium thiosulfate one drop at a time until the blue colour disappears.
- When this happens, it means all the iodine has just reacted.
- Record the volume of sodium thiosulfate added to the solution.

Ideally, you should repeat steps 1 and 2 until you get three concordant results. Then you can work out a mean titre value to use in steps 3 and 4.

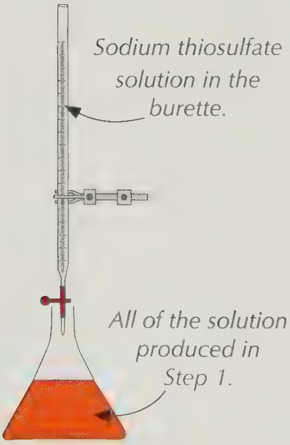

Sodium thiosulfate solution in the burette.
All of the solution produced in Step 1.

***Figure 1:** The apparatus used to perform an iodine-sodium thiosulfate titration.*

Step 3: Calculate the number of moles of iodine present

To do this you need to:

- Calculate the number of moles of thiosulfate ions used in the titration.
- Then use the 1 : 2 molar ratio of $I_2 : S_2O_3^{2-}$ in the balanced equation for the reaction (shown in Step 2) to work out how many moles of iodine were present in the solution.

Step 4: Calculate the concentration of the oxidising agent

This bit's the same as the last few steps for a redox titration (see page 390).

- Use the 3 : 1 molar ratio of $I_2 : IO_3^-$ from the balanced equation in step 1 to work out how many moles of iodate(V) ions were present in the solution.
- You can then use this to work out the concentration of potassium iodate(V).

Example — **Maths Skills**

25.0 cm^3 of potassium iodate(V) solution was added to an excess of acidified potassium iodide. This solution was then titrated against a 0.120 mol dm^{-3} solution of sodium thiosulfate. 11.1 cm^3 of thiosulfate solution was required to react fully with the solution.
Find the concentration of the potassium iodate(V) solution.

Because you're given the titration data in the question you can start at step 3 for this one:

First calculate the number of moles of thiosulfate ions used in the titration...

$$\text{Number of moles of thiosulfate} = \frac{\text{concentration} \times \text{volume (cm}^3\text{)}}{1000}$$

$$= \frac{0.120 \times 11.1}{1000}$$

$$= 1.332 \times 10^{-3} \text{ moles}$$

Then use the balanced equation and the molar ratio to calculate the number of moles of iodine in the solution.

Balanced equation: $I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$

1 mole of iodine reacts with 2 moles of thiosulfate. So,

Number of moles of iodine in the solution = $1.332 \times 10^{-3} \div 2$

$= 6.66 \times 10^{-4}$ moles

Now do step 4: Look at the balanced equation for the reaction of iodate ions with acidified iodide ions. Use the molar ratio from this equation to calculate the number of moles of potassium iodate(V) present in the solution.

Balanced equation: $IO_3^-{}_{(aq)} + 5I^-{}_{(aq)} + 6H^+{}_{(aq)} \rightarrow 3I_{2\,(aq)} + 3H_2O$

25.0 cm^3 of potassium iodate(V) solution produced 6.66×10^{-4} moles of iodine. The equation shows that one mole of iodate(V) ions will produce three moles of iodine.

That means there must have been $(6.66 \times 10^{-4}) \div 3 = 2.22 \times 10^{-4}$ moles of iodate(V) ions in the original solution. So now it's straightforward to find the concentration of the potassium iodate(V) solution, which is what you're after:

$$\text{concentration of iodate(V) ions} = \frac{\text{number of moles} \times 1000}{\text{volume (cm}^3\text{)}}$$

$$= \frac{2.22 \times 10^{-4} \times 1000}{25.0}$$

$$\text{concentration of } KIO_3 = \mathbf{0.00888 \text{ mol dm}^{-3}}$$

You don't have to use potassium iodate(V) solution (KIO_3) as the oxidising agent for this reaction — the method works the same way with any oxidising agent.

In fact, you may have to answer questions in the exams involving redox titration systems you've not met before. Just follow the same method as shown on the last few pages, and you'll be fine.

Figure 2: *Titrating iodine with sodium thiosulfate.*

Tip: Don't forget that in step 3 and step 4 you are using different balanced equations and different molar ratios. First you need to calculate the number of moles of iodine then you can use this information to calculate the moles of iodate(V) ions.

Tip: This is just the formula:
moles = conc. × volume
rearranged to give:
conc. = moles ÷ volume

Tip: Always remember to give units with your answer. It'd be crazy to get through all those steps just to lose marks 'cause you didn't put down your units.

Practice Questions — Application

Q1 13.2 cm^3 of potassium iodate(V) solution was added to an excess of acidified potassium iodide, and the following reaction occurred: $IO_3^-{}_{(aq)} + 5I^-{}_{(aq)} + 6H^+{}_{(aq)} \rightarrow 3I_{2\,(aq)} + 3H_2O_{(l)}$.
The solution formed by this reaction was then titrated against a 0.200 mol dm^{-3} solution of sodium thiosulfate. 41.1 cm^3 of thiosulfate solution was required to react fully with the solution. Here's the equation for this reaction: $I_{2\,(aq)} + 2Na_2S_2O_{3\,(aq)} \rightarrow 2NaI_{(aq)} + Na_2S_4O_{6\,(aq)}$

a) Calculate the number of moles of sodium thiosulfate used in the reaction.

b) Calculate the number of moles of iodine formed by adding the potassium iodate(V) solution to the acidified potassium iodide.

c) Work out the number of moles of potassium iodate present.

d) Work out the concentration of the potassium iodate(V) solution used in this experiment.

Q2 39.0 cm^3 of potassium manganate(VII) solution was added to 61.0 cm^3 (an excess) of acidified potassium iodide. 25.0 cm^3 of this solution was then titrated against a 0.750 mol dm^{-3} solution of sodium thiosulfate. 4.00 cm^3 of thiosulfate solution was required to react fully with the solution. Here are the reactions that occur in this experiment:

$$2MnO_4^-{}_{(aq)} + 10I^-{}_{(aq)} + 16H^+{}_{(aq)} \rightarrow 5I_{2\,(aq)} + 8H_2O_{(l)} + 2Mn^{2+}{}_{(aq)}$$
$$I_{2\,(aq)} + 2Na_2S_2O_{3\,(aq)} \rightarrow 2NaI_{(aq)} + Na_2S_4O_{6\,(aq)}$$

Tip: For Q2 b) it's important to remember that the total volume of the reaction mixture was 39.0 + 61.0 = 100 cm^3, but that only 25 cm^3 of this solution was then used in the titration.

a) Calculate the number of moles of sodium thiosulfate used in the reaction.

b) Calculate the total number of moles of iodine formed by adding the potassium manganate(VII) solution to the acidified potassium iodide.

c) Work out the concentration of the potassium manganate(VII) solution used in this experiment.

Q3 15.0 cm^3 of potassium dichromate(VI) solution was added to an excess of acidified potassium iodide. This solution was then titrated against a 0.0600 mol dm^{-3} solution of sodium thiosulfate. If 22.3 cm^3 of sodium thiosulfate solution was required to react fully with the solution, what was the concentration of the potassium dichromate(VI) solution?

Here are the equations for the two steps of the experiment:

$$Cr_2O_7^{2-}{}_{(aq)} + 6I^-{}_{(aq)} + 14H^+{}_{(aq)} \rightarrow 2Cr^{3+}{}_{(aq)} + 3I_{2\,(aq)} + 7H_2O_{(l)}$$
$$I_{2\,(aq)} + 2S_2O_3^{2-}{}_{(aq)} \rightarrow 2I^-{}_{(aq)} + S_4O_6^{2-}{}_{(aq)}$$

Exam Tip
In your exams you could be asked to complete a calculation like this one step at a time, or you could be dumped in at the deep end and asked to do the whole calculation (like in Q3). So you need to be really clear on how to work through them.

Practice Questions — Fact Recall

Q1 Write out the ionic equation for a reaction between iodate(V) ions, and acidified potassium iodide solution.

Q2 Write down the ionic equation for the reaction between iodine and thiosulfate ions.

Q3 Describe how you would carry out a titration between an iodine solution and sodium thiosulfate.

Tip: Remember, you need to know how to carry out the titrations as well as how to do all the titration calculations.

4. Electrochemical Cells

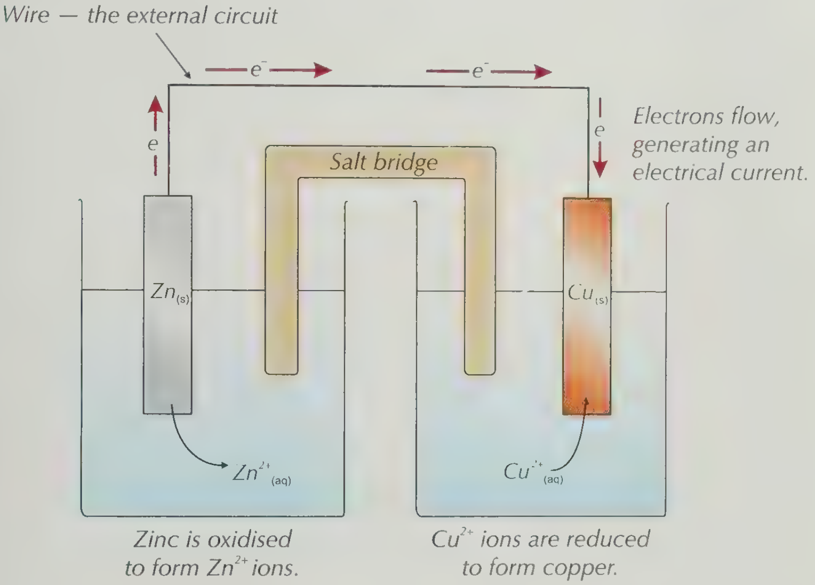
In redox reactions, electrons move from one atom to another. When electrons move, you get an electrical current. So redox reactions can be used to generate electricity.

What are electrochemical cells?

Electrochemical cells can be made from two different metals dipped in salt solutions of their own ions and connected by a wire (the external circuit). There are always two reactions within an electrochemical cell — one's an oxidation and one's a reduction — so it's a **redox** process.

Example

The diagram below shows an electrochemical cell made using copper and zinc.


Wire — the external circuit
e^-
e^-
e
e
Electrons flow, generating an electrical current.
Salt bridge
$Zn_{(s)}$
$Cu_{(s)}$
$Zn^{2+}_{(aq)}$
$Cu^{2+}_{(aq)}$
Zinc is oxidised to form Zn^{2+} ions.
Cu^{2+} ions are reduced to form copper.

A copper electrode is dipped in a solution of Cu^{2+} ions and a zinc electrode is dipped in a solution of Zn^{2+} ions. Zinc loses electrons more easily than copper. So in the half-cell on the left, zinc (from the zinc electrode) is oxidised to form $Zn^{2+}_{(aq)}$ ions. This releases electrons into the external circuit. In the other half-cell, the same number of electrons are taken from the external circuit, reducing the Cu^{2+} ions to copper atoms.

The solutions are connected by a **salt bridge**, e.g. a strip of filter paper soaked in $KNO_{3(aq)}$. This allows ions to flow through and balance out the charges — it completes the circuit.

Electrons flow through the wire from the more reactive metal to the less reactive metal. You can put a voltmeter in the external circuit to measure the voltage between the two half-cells. This is the **cell potential** or e.m.f., E_{cell}.

You can also have half-cells involving solutions of aqueous ions of the same element with different oxidation numbers.

Learning Objectives:

- Know the techniques and procedures used for the measurement of cell potentials of metals or non-metals in contact with their ions in aqueous solution (PAG 8).
- Know the techniques and procedures used for the measurement of cell potentials of ions of the same element in different oxidation states in contact with a Pt electrode (PAG 8).

Specification Reference 5.2.3

Tip: See pages 385-387 for more on redox reactions.

Figure 1: *An electrochemical cell.*

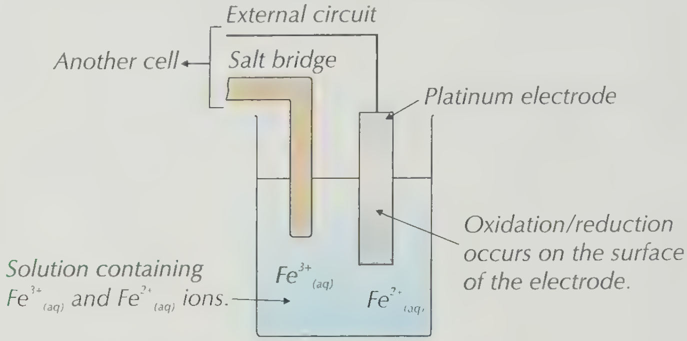
Tip: The two different sides of the electrochemical cell are called half-cells — two half-cells make a whole.

Tip: e.m.f. stands for electromotive force.

Tip: An electrode has to be a solid that conducts electricity. If a half-cell doesn't contain anything like this, as in this example, you can use something else as the electrode. But it must be inert too — this means it won't react with any of the solutions in the cell. You'd usually use an electrode made from platinum or graphite.

Example

You can make an electrochemical half-cell using solutions of Fe^{2+} and Fe^{3+} ions. A platinum electrode is dipped into the solution.


External circuit
Another cell
Salt bridge
Platinum electrode
Oxidation/reduction occurs on the surface of the electrode.
Solution containing $Fe^{3+}_{(aq)}$ and $Fe^{2+}_{(aq)}$ ions.
$Fe^{3+}_{(aq)}$
$Fe^{2+}_{(aq)}$

When this half-cell is connected to another half-cell, a current will flow and $Fe^{2+}_{(aq)}$ will be converted to $Fe^{3+}_{(aq)}$ or vice versa. The conversion of $Fe^{2+}_{(aq)}$ to $Fe^{3+}_{(aq)}$ (or Fe^{3+} to Fe^{2+}) happens on the surface of the platinum electrode.

The direction of the conversion depends on the other half-cell in the circuit. If the other cell contains a metal that is less reactive than iron then Fe^{2+} will be oxidised to Fe^{3+} at the electrode. But if the other cell contains a metal that is more reactive than iron, then Fe^{3+} will be reduced to Fe^{2+} at the electrode.

Tip: Remember to carry out a risk assessment before starting any experiment.

You can also use non-metals, like chlorine or hydrogen, as reactants in electrochemical cells. For systems involving a gas, the gas can be bubbled over an inert electrode (for example, a platinum electrode) sitting in a solution of its aqueous ions (e.g. Cl^- or H^+). This is the technique used to create a standard hydrogen electrode (see page 399).

Measuring the voltage of an electrochemical cell

PRACTICAL ACTIVITY GROUP 8

Tip: Setting up an electrochemical cell involving non-metals can be a bit harder. You may need a platinum or graphite electrode and a stream of gas of the non-metal you're investigating.

Tip: If you're creating an electrochemical cell where one of the species you're investigating involves two ions (e.g. $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$), then you'll need to use a platinum electrode and a solution containing both ions.

You need to know how to set up an electrochemical cell and use it to take measurements of voltage. Here's a method you can use to construct an electrochemical cell involving two metals.

1. Get a strip of each of the metals you're investigating. These are your electrodes. Clean the surfaces of the metals using a piece of emery paper (or sandpaper).
2. Clean any grease or oil from the electrodes using some propanone. From this point on, be careful not to touch the surfaces of the metals with your hands — you could transfer grease back onto the strips.
3. Place each electrode into a beaker filled with a solution containing ions of that metal. For example, if you had an electrode made of zinc metal, you could place it in a beaker of $ZnSO_{4\,(aq)}$. If you had an electrode made of copper, you could use a solution of $CuSO_{4\,(aq)}$.
4. Create a salt bridge to link the two solutions together. You can do this by simply soaking a piece of filter paper in a salt solution, e.g. $KCl_{(aq)}$ or $KNO_{3\,(aq)}$, and draping it between the two beakers. The ends of the filter paper should be immersed in the solutions.
5. Connect the electrodes to a voltmeter, using crocodile clips and wires. If you've set up your circuit correctly, you'll get a reading on your voltmeter.

You can carry out various investigations using this basic set-up. By changing the materials the electrodes are made of and the solutions which they sit in, or varying the concentration of the solutions used, you can measure how the cell potential varies.

If you perform your experiment under **standard conditions**, the voltage that you measure will be the standard cell potential ($E^{\ominus}_{cell}$) for that cell. There's more about the standard conditions used for measuring electrode potentials on page 399. For now, just remember that if you're asked how you would set up an experiment to measure standard cell potential, you must say that the experiment would be performed at 298 K, a pressure of 100 kPa and with all the solutions at a concentration of 1.00 mol dm^{-3}.

Electrode potentials

The reactions that occur at each electrode in a cell are reversible.

Example

The reactions that occur at each electrode in the zinc/copper cell are:

$$Zn^{2+}_{(aq)} + 2e^- \rightleftharpoons Zn_{(s)}$$
$$Cu^{2+}_{(aq)} + 2e^- \rightleftharpoons Cu_{(s)}$$

The reversible arrows show that both reactions can go in either direction.

Tip: These are half-equations for the reactions occurring in the electrochemical cell. See pages 385-386 for more on half-equations.

Which direction each reaction goes in depends on how easily each metal loses electrons (i.e. how easily it's oxidised). How easily a metal is oxidised is measured using **electrode potentials**. A metal that's easily oxidised has a very negative electrode potential, while one that's harder to oxidise has a less negative (or positive) electrode potential.

Example

The table below shows the electrode potentials for the copper and zinc half-cells:

Half-cell	Electrode potential / V
$Zn^{2+}_{(aq)}/Zn_{(s)}$	–0.76
$Cu^{2+}_{(aq)}/Cu_{(s)}$	+0.34

The zinc half-cell has a more negative electrode potential, so in a zinc/copper cell, zinc is oxidised (the reaction goes backwards), while copper is reduced (the reaction goes forwards).

Figure 2: Analogue or digital voltmeters can be used to measure electrode potentials.

Tip: There's more on how standard electrode potentials are measured coming up.

Practice Questions — Application

Q1 The following reactions occur in an electrochemical cell:

$$Ni^{2+}_{(aq)} + 2e^- \rightleftharpoons Ni_{(s)} \qquad E^{\ominus} = -0.25$$
$$Cu^{2+}_{(aq)} + 2e^- \rightleftharpoons Cu_{(s)} \qquad E^{\ominus} = +0.34$$

a) Draw and label a diagram showing how this electrochemical cell could be set up.

b) Which of the reactions above will go in the direction of oxidation in this electrochemical cell?

Exam Tip
You don't have to memorise values for electrode potentials. You'll always be told them in the question.

Q2 An electrochemical cell containing a calcium half-cell and a silver half-cell was set up using a salt bridge.

Half-cell	Electrode potential / V
$Ca^{2+}_{(aq)}/Ca_{(s)}$	–2.87
$Ag^{+}_{(aq)}/Ag_{(s)}$	+0.80

a) Write a half-equation for the reduction reaction that will happen in this cell.

b) Write a half-equation for the oxidation reaction that will happen in this cell.

Q3 In an electrochemical cell with a $Mg^{2+}_{(aq)}/Mg_{(s)}$ half-cell and a $Fe^{3+}_{(aq)}/Fe^{2+}_{(aq)}$ half-cell (using a Pt electrode), oxidation occurs in the $Mg^{2+}_{(aq)}/Mg_{(s)}$ half-cell and reduction in the $Fe^{3+}_{(aq)}/Fe^{2+}_{(aq)}$ half-cell. State which half-cell has the more negative electrode potential.

Practice Questions — Fact Recall

Q1 a) Suggest a substance that could be used for the electrode in a half-cell involving solutions of two aqueous ions of the same element.

b) Explain why the substance you have named is suitable for this use.

Q2 Two half-cells are joined to form an electrochemical cell. A salt bridge, made from filter paper soaked in $KNO_{3(aq)}$, is put between the half-cells. A voltmeter is placed in the external circuit of the cell.

a) What is the purpose of the salt bridge?

b) What does the reading on the voltmeter tell you?

Q3 In an electrochemical cell, will oxidation or reduction occur in the half-cell with the more positive electrode potential?

Q4 If you have two metals, one of which is very easy to oxidise and the other of which is difficult to oxidise, which metal will have the more negative electrode potential?

5. Standard Electrode Potentials

Electrode potentials are influenced by things like temperature and pressure. So if you want to compare electrode potentials, they need to be standardised. This is done using a standard hydrogen electrode.

Learning Objectives:

- Be able to use the term *standard electrode* (redox) *potential*, $E^{\ominus}$.
- Know how to measure the standard electrode (redox) potential, $E^{\ominus}$, using a hydrogen electrode.

Specification Reference 5.2.3

Factors affecting the electrode potential

Half-cell reactions are reversible. So just like any other reversible reaction, the equilibrium position is affected by changes in temperature, pressure and concentration. Changing the equilibrium position changes the cell potential. To get around this, **standard conditions** are used to measure electrode potentials — using these conditions means you always get the same value for the electrode potential and you can compare values for different cells.

Tip: See pages 331-332 for more on how changes in concentration temperature and pressure affect the position of equilibrium.

Measuring standard electrode potentials

The standard electrode potential of a half-cell is the voltage measured under standard conditions when the half-cell is connected to a **standard hydrogen electrode**. The standard electrode potential of the hydrogen cell is given the value of 0.00 V. So, the voltage reading of the whole cell is equal to the standard electrode potential of whatever your hydrogen half-cell is attached to.

In the standard hydrogen electrode, hydrogen gas is bubbled into a solution of aqueous H^+ ions. A platinum foil electrode is used as a platform for the oxidation/reduction reactions — see Figure 1.

Tip: Electrode potentials can also be called 'redox potentials'. So, standard electrode potentials are also called standard redox potentials. Easy, huh?

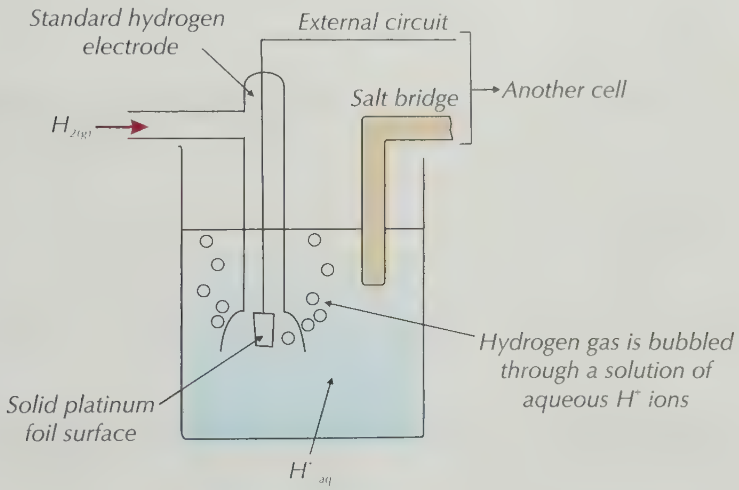

Standard hydrogen electrode
External circuit
Another cell
Salt bridge
$H_{2(g)}$
Hydrogen gas is bubbled through a solution of aqueous H^+ ions
Solid platinum foil surface
H^+_{aq}

Figure 1: *The standard hydrogen electrode*

When measuring electrode potentials using the standard hydrogen electrode it is important that everything is done under standard conditions:

1. Any solutions of ions must have a concentration of 1.00 mol dm^{-3}.
2. The temperature must be 298 K (25 °C).
3. The pressure must be 100 kPa.

If standard conditions are maintained, the reading on the voltmeter when a half-cell is connected to the standard hydrogen electrode will be the standard electrode potential of that half-cell — see Figure 2.

Tip: The reading on the voltmeter could be positive or negative, depending on which way the electrons flow.

Tip: Notice how the pressure is 100 kPa, the temperature is 298 K and the H^+ and Zn^{2+} solutions both have concentrations of 1.00 mol dm^{-3}. These are the standard conditions.

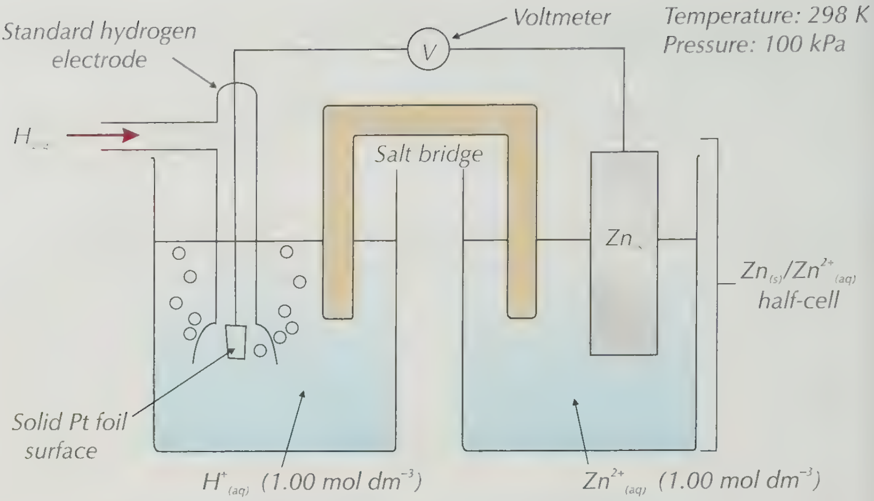

Standard hydrogen electrode
Voltmeter
V
Temperature: 298 K
Pressure: 100 kPa
$H_{2(g)}$
Salt bridge
$Zn_{(s)}$
$Zn_{(s)}/Zn^{2+}_{(aq)}$ half-cell
Solid Pt foil surface
$H^+_{(aq)}$ (1.00 mol dm^{-3})
$Zn^{2+}_{(aq)}$ (1.00 mol dm^{-3})

Figure 2: *Measuring the standard electrode potential of a $Zn_{(s)}/Zn^{2+}_{(aq)}$ half-cell.*

Exam Tip
You could also be asked to draw a diagram of a set-up you could use to measure the standard cell potential of an electrochemical cell. Just follow all these rules, but swap the standard hydrogen electrode for a different half-cell.

In the exams, you could be asked to draw a diagram showing how the standard electrode potential of a particular half-cell could be measured. If you are, just remember these things:

- Always put the standard hydrogen electrode on the left.
- Make sure you draw a complete circuit — don't forget to include the salt bridge, the wire between the electrodes and the voltmeter.
- Label any solutions as being 1.00 mol dm^{-3}.
- If your half-cell contains aqueous ions of the same element in different oxidation numbers, don't forget to include a platinum electrode.

Practice Question — Application

Q1 When a $Pb^{2+}_{(aq)}/Pb_{(s)}$ half-cell under standard conditions was connected to a standard hydrogen electrode via a voltmeter, the reading on the voltmeter was –0.13 V.

a) What was the concentration of the Pb^{2+} solution in the $Pb^{2+}_{(aq)}/Pb_{(s)}$ half-cell

b) What is the standard electrode potential of the Pb^{2+}/Pb half-cell?

Practice Questions — Fact Recall

Q1 Give three factors that can influence electrode potentials.

Q2 Describe how a standard hydrogen electrode is set up and give the standard conditions used when measuring electrode potentials.

Q3 What is the electrode potential of the standard hydrogen electrode?

6. Electrochemical Series

The standard electrode potentials of different reactions are different (unsurprisingly). If you write a list of electrode potentials in order, you get an electrochemical series, which you can use to predict the outcome of a reaction.

Learning Objectives:

- Be able to calculate a standard cell potential by combining two standard electrode potentials.
- Be able to predict the feasibility of a reaction using standard cell potentials.
- Know the limitations of predictions about the feasibility of reactions, made using standard cell potentials, in terms of kinetics and concentration.

Specification Reference 5.2.3

What is an electrochemical series?

An **electrochemical series** is basically a big long list of electrode potentials for different electrochemical half-cells. They look something like this:

Half-reaction	$E^\ominus$ / V
$Mg^{2+}_{(aq)} + 2e^- \rightleftharpoons Mg_{(s)}$	–2.37
$Al^{3+}_{(aq)} + 3e^- \rightleftharpoons Al_{(s)}$	–1.66
$Zn^{2+}_{(aq)} + 2e^- \rightleftharpoons Zn_{(s)}$	–0.76
$Ni^{2+}_{(aq)} + 2e \rightleftharpoons Ni_{(s)}$	–0.25
$2H^+_{(aq)} + 2e^- \rightleftharpoons H_{2\,(g)}$	0.00
$Sn^{4+}_{(aq)} + 2e^- \rightleftharpoons Sn^{2+}_{(aq)}$	+0.15
$Cu^{2+}_{(aq)} + 2e^- \rightleftharpoons Cu_{(s)}$	+0.34
$Fe^{3+}_{(aq)} + e^- \rightleftharpoons Fe^{2+}_{(aq)}$	+0.77
$Ag^+_{(aq)} + e^- \rightleftharpoons Ag_{(s)}$	+0.80
$Br_{2(l)} + 2e^- \rightleftharpoons 2Br^-_{(aq)}$	+1.09
$Cr_2O_7{}^{2-}_{(aq)} + 14H^+_{(aq)} + 6e^- \rightleftharpoons 2Cr^{3+}_{(aq)} + 7H_2O_{(l)}$	+1.33
$Cl_{2(g)} + 2e^- \rightleftharpoons 2Cl^-_{(aq)}$	+1.36
$MnO_4{}^-_{(aq)} + 8H^+_{(aq)} + 5e^- \rightleftharpoons Mn^{2+}_{(aq)} + 4H_2O_{(l)}$	+1.52

Figure 1: *A table showing an electrochemical series.*

Exam Tip
Don't panic — you don't have to memorise any of these values. You'll always be told them in the question if you need to use them.

The electrode potentials are written in order, starting from the most negative and going down to the most positive. The half-equations are always written as reduction reactions — but the reactions are reversible and can go the opposite way. When two half-equations are put together in an electrochemical cell, the one with the more negative electrode potential goes in the direction of oxidation (backwards) and the one with the more positive electrode potential goes in the direction of reduction (forwards).

Calculating cell potentials

You can use the information in an electrochemical series to calculate the **standard cell potential** ($E^\ominus_{cell}$) or **e.m.f.**, when two half-cells are connected together. All you have to do is work out which half-reaction is going in the direction of oxidation and which half-reaction is going in the direction of reduction. Then just substitute the $E^\ominus$ values into this equation:

$$E^\ominus_{cell} = E^\ominus_{reduced} - E^\ominus_{oxidised}$$

This is the standard electrode potential of the half-cell which goes in the direction of reduction (the one with the more positive electrode potential).

This is the standard electrode potential of the half-cell which goes in the direction of oxidation (the one with the more negative electrode potential).

Tip: You can use a standard hydrogen electrode to work out standard electrode potentials (see page 399 for more details).

Tip: Don't forget — cell potential is the voltage between two half-cells. See page 395 for more.

Tip: If $E^\ominus_{cell}$ is positive, the reaction is feasible (it could happen). There's more about this coming up on the next page.

Example **Maths Skills**

Calculate the standard cell potential of an Mg/Ag electrochemical cell using the two half-equations shown below:

$$Mg^{2+}_{(aq)} + 2e^- \rightleftharpoons Mg_{(s)} \qquad E^\ominus = -2.37$$

$$Ag^{+}_{(aq)} + e^- \rightleftharpoons Ag_{(s)} \qquad E^\ominus = +0.80$$

The Mg/Mg^{2+} half-cell has the more negative electrode potential, so this half reaction will go in the direction of oxidation. The Ag/Ag^+ half-cell has the more positive electrode potential and so will go in the direction of reduction.

$$E^\ominus_{cell} = E^\ominus_{reduced} - E^\ominus_{oxidised} = 0.80 - (-2.37) = \mathbf{+3.17\ V}$$

Tip: If you can't remember which half-reaction in a cell goes backwards and which goes forwards, think NO P.R. — the more Negative electrode potential will go in the Oxidation direction and the more Positive electrode potential will go in the Reduction direction.

Predicting the direction of reactions

You can use electrode potentials to predict whether a redox reaction will happen and to show which direction it will go in. Just follow these steps:

1. Find the two half-equations for the redox reaction, and write them both out as reduction reactions.
2. Use an electrochemical series to work out which half-equation has the more negative electrode potential.
3. Write out the half-equation with the more negative electrode potential going in the backwards direction (oxidation) and the half-equation with the more positive electrode potential going in the forwards direction (reduction).
4. Combine the two half-equations and write out a full redox equation.

Tip: Once you know these steps, you can apply them to predict the outcome of any redox reaction.

This is the feasible direction of the reaction and will give a positive overall $E^\ominus$ value. The reaction will not happen the other way round.

Example

Predict the direction of the reaction when a Zn/Zn^{2+} half-cell is connected to a Cu^{2+}/Cu half-cell.

1. Write down the two half-equations for the redox reaction as reduction reactions:

$$Zn^{2+}_{(aq)} + 2e^- \rightleftharpoons Zn_{(s)} \quad \text{and} \quad Cu^{2+}_{(aq)} + 2e^- \rightleftharpoons Cu_{(s)}$$

2. Look up the electrode potentials for the two half-equations:

$$Zn^{2+}_{(aq)} + 2e^- \rightleftharpoons Zn_{(s)} \qquad E^\ominus = -0.76\ V$$

$$Cu^{2+}_{(aq)} + 2e^- \rightleftharpoons Cu_{(s)} \qquad E^\ominus = +0.34\ V$$

Tip: These values for the electrode potentials came from the electrochemical series on page 401.

3. The zinc half-reaction has the more negative electrode potential so write it out going backwards and the copper half-reaction going forwards.

$$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$$

$$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$$

4. Combine the half-equations to give the full redox equation:

$$Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$$

This full equation shows you the direction of the reaction — zinc metal will reduce copper(II) ions and copper(II) ions will oxidise zinc metal.

Tip: If you can't remember how to combine half-equations, have a look at pages 385-387.

Just to back this up, if you calculate $E^\ominus_{cell}$ for this reaction...

$$E^\ominus_{cell} = E^\ominus_{reduced} - E^\ominus_{oxidised} = 0.34 - (-0.76) = +1.1\text{ V}$$

...you'll see that it's positive — so the reaction is feasible. By contrast, zinc(II) ions will not oxidise copper metal — this reaction would have a cell potential of –1.1 V.

You could also be given a reaction and asked whether or not it is feasible. If this is the case, you can follow the same method — just use the half-equations and the electrode potentials to work out the feasible direction of the reaction and see if it matches the direction given in the question.

Example

Predict whether copper will react with aqueous nickel ions.

First, find the two half-equations that would make up this reaction in an electrochemical series. Write them both out as reduction reactions:

$$Ni^{2+}_{(aq)} + 2e^- \rightleftharpoons Ni_{(s)} \qquad E^\ominus = -0.25\text{ V}$$

$$Cu^{2+}_{(aq)} + 2e^- \rightleftharpoons Cu_{(s)} \qquad E^\ominus = +0.34\text{ V}$$

The Ni/Ni^{2+} half-cell has the more negative electrode potential, so it will go in the direction of oxidation: $Ni_{(s)} \rightarrow Ni^{2+}_{(aq)} + 2e^-$

The Cu/Cu^{2+} half-cell has the more positive electrode potential, so it will go in the direction of reduction: $Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$

These two half-equations combine to give: $Ni_{(s)} + Cu^{2+}_{(aq)} \rightarrow Ni^{2+}_{(aq)} + Cu_{(s)}$

This shows the feasible direction of this reaction. It does not match the reaction described in the question, so copper will not react with nickel ions.

Problems with predicting reactions

A prediction using $E^\ominus$ will only tell you if a reaction is possible under standard conditions. The prediction might be wrong if...

Tip: Remember — just because a reaction is feasible doesn't mean that it will actually happen.

...the conditions are not standard

Changing the concentration (or temperature) of the solutions can cause the electrode potential to change. For example, the zinc/copper cell has these half equations in equilibrium:

$$Zn_{(s)} \rightleftharpoons Zn^{2+}_{(aq)} + 2e^-$$

$$Cu^{2+}_{(aq)} + 2e^- \rightleftharpoons Cu_{(s)}$$

If you increase the concentration of Zn^{2+}, that equilibrium will shift to the left, reducing the ease of electron loss. This will make the cell potential lower. If you increase the concentration of Cu^{2+}, that equilibrium will shift to the right, increasing the ease of electron gain. This will make the cell potential higher.

...the reaction kinetics are not favourable

The rate of a reaction may be so slow that the reaction might not appear to happen. Also, if a reaction has a high activation energy, this may stop it happening.

Tip: You'll find the electrode potentials that you need to answer these questions in the electrochemical series on page 401.

Practice Questions — Application

Q1 Calculate $E^\ominus_{cell}$ for the following reactions:

a) $Al_{(s)} + 3Ag^+_{(aq)} \rightarrow Al^{3+}_{(aq)} + 3Ag_{(s)}$

b) $Cu_{(s)} + Cl_{2(g)} \rightarrow Cu^{2+}_{(aq)} + 2Cl^-_{(aq)}$

c) $Sn^{2+}_{(aq)} + 2Fe^{3+}_{(aq)} \rightarrow Sn^{4+}_{(aq)} + 2Fe^{2+}_{(aq)}$

Q2 State whether or not these reactions are feasible:

a) $Mg_{(s)} + Ni^{2+}_{(aq)} \rightarrow Mg^{2+}_{(aq)} + Ni_{(s)}$

b) $2Br^-_{(aq)} + 2Fe^{3+}_{(aq)} \rightarrow 2Fe^{2+}_{(aq)} + Br_{2\,(l)}$

c) $Sn^{2+}_{(aq)} + Cu^{2+}_{(aq)} \rightarrow Sn^{4+}_{(aq)} + Cu_{(s)}$

Q3 Will Ag^+ ions react with Sn^{2+} ions in solution? Explain your answer.

Practice Questions — Fact Recall

Q1 What is an electrochemical series?

Q2 In what direction are half-equations written in electrochemical series?

Q3 A half-reaction has a very positive electrode potential. Is it more likely to go in the direction of oxidation or reduction?

Q4 Give two reasons why a prediction made about the feasibility of a reaction using $E^\ominus_{cell}$ might be wrong.

7. Energy Storage Cells

The last few topics told you all about electrochemical cells. This one's all about what electrochemical cells are actually used for — in particular, how electrochemical cells are used as energy storage cells (batteries).

What are energy storage cells?

Energy storage cells (batteries) have been around for ages and modern ones work just like an electrochemical cell. For example the nickel-iron cell was developed way back at the start of the 1900s and is often used as a back-up power supply because it can be repeatedly charged and is very robust.

You can work out the voltage produced by these cells by using the electrode potentials of the substances used in the cell. There are lots of different cells and you won't be asked to remember the $E^\ominus$ for the reactions, but you might be asked to work out the cell potential (voltage) for a given cell... so here's an example I prepared earlier.

Example

The nickel-iron cell has a nickel oxide hydroxide (NiOOH) cathode and an iron (Fe) anode with potassium hydroxide as the electrolyte. Using the half-equations given:

a) write out the full equation for the reaction.

b) calculate the voltage produced by the nickel-iron cell.

$$Fe(OH)_2 + 2e^- \rightleftharpoons Fe + 2OH^- \qquad E^\ominus = -0.44\ V$$

$$NiOOH + H_2O + e^- \rightleftharpoons Ni(OH)_2 + OH^- \qquad E^\ominus = +0.76\ V$$

a) First work out which half-equation will go in the forward (reduction) direction and which in the reverse (oxidation) direction. The iron half-equation has the more negative electrode potential, so it will go in the direction of oxidation: $Fe + 2OH^- \rightleftharpoons Fe(OH)_2 + 2e^-$
The other half-equation will go in the direction of reduction:
$NiOOH + H_2O + e^- \rightleftharpoons Ni(OH)_2 + OH^-$

Now to find the overall equation for the reaction, just balance the number of electrons and then combine the two half-equations.

$$2NiOOH + 2H_2O + Fe \rightleftharpoons 2Ni(OH)_2 + Fe(OH)_2$$

(The e^- and the OH^- are not shown because they cancel out.)

b) To calculate the voltage you use the same formula that you use to work out cell potential (see page 401). So the voltage is...

$$E^\ominus_{cell} = E^\ominus_{reduced} - E^\ominus_{oxidised}$$
$$= +0.76 - (-0.44) = \mathbf{1.2\ V}$$

Recharging energy storage cells

Some energy storage cells, like the nickel-iron cell, are rechargeable. Rechargeable energy storage cells can be recharged because the reactions that occur within them are reversible. To recharge these batteries, a current is supplied to force electrons to flow in the opposite direction around the circuit and reverse the reactions. This is possible because none of the substances in a rechargeable battery escape or are used up. In the exam you could be asked to write equations for the reaction that occurs when an energy storage cell is recharged. These are just the equations for the storage cell in reverse.

Learning Objectives:

- Be able to apply principles of electrode potentials to modern storage cells.
- Know the benefits and risks of electrochemical cells.

Specification Reference 5.2.3

Tip: Anode and cathode are just names for the electrodes in an electrochemical cell.

Figure 1: *An assortment of batteries — these are all electrochemical cells.*

Tip: See pages 385-387 for more on combining half-equations into full equations.

Figure 2: *A lithium ion battery being recharged.*

Example

When the nickel-iron cell is recharged, the half-equations for the reaction are:

$$Fe(OH)_2 + 2e^- \rightleftharpoons Fe + 2OH^-$$

$$Ni(OH)_2 + OH^- \rightleftharpoons NiOOH + H_2O + e^-$$

So, the overall equation when a nickel-iron cell is recharged is:

$$2Ni(OH)_2 + Fe(OH)_2 \rightleftharpoons 2NiOOH + 2H_2O + Fe$$

Tip: When an energy storage cell is being used, the cell is discharging — this is the opposite of recharging the cell.

Benefits and risks of electrochemical cells

HOW SCIENCE WORKS

Electrochemical cells have many advantages — they can be cheap to make and have relatively high power densities (a small cell can produce a lot of energy).

However, the production of the cells involves the use of toxic chemicals, which need to be disposed of once the cell has reached the end of its life span. The chemicals used to make the cells are also often very flammable. E.g. lithium (commonly used in rechargeable batteries) is highly reactive and will catch fire if a fault causes it to overheat.

Tip: Choosing energy supplies is often a case of weighing up the risks and benefits associated with the manufacture, use and disposal of the fuel and its casing.

HOW SCIENCE WORKS

Practice Questions — Application

Q1 Nickel/cadmium batteries are a common type of rechargeable battery. The redox equation for the reaction that happens when this type of battery is discharging is shown below:

$$Cd_{(s)} + 2NiOOH_{(s)} + 2H_2O_{(l)} \rightleftharpoons Cd(OH)_{2(s)} + 2Ni(OH)_{2(s)} \quad E^{\ominus} = +1.4\text{ V}$$

Suggest an equation for the redox reaction that occurs when this type of battery is recharging.

Q2 Zinc-carbon dry cell batteries are commonly used in TV remote controls and torches. The half-equations for the reactions that occur when this type of battery is discharging are shown below:

$$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^- \quad E^{\ominus} = -0.76\text{ V}$$

$$2MnO_{2(s)} + 2NH_4{}^+_{(aq)} + 2e^- \rightarrow Mn_2O_{3(s)} + 2NH_{3(aq)} + H_2O_{(l)} \quad E^{\ominus} = +0.75\text{ V}$$

a) Calculate $E^{\ominus}_{cell}$ for this cell.

b) Write an equation for the overall reaction occurring in this cell.

Q3 Lead-acid cells are used in car batteries. The half-equations for the two half-cells used to make this type of battery are shown below:

$$PbSO_{4(s)} + 2e^- \rightleftharpoons Pb_{(s)} + SO_4{}^{2-}_{(aq)} \quad E^{\ominus} = -0.36\text{ V}$$

$$PbO_{2(s)} + SO_4{}^{2-}_{(aq)} + 4H^+_{(aq)} + 2e^- \rightleftharpoons PbSO_{4(s)} + 2H_2O_{(l)} \quad E^{\ominus} = +1.69\text{ V}$$

Write half-equations for the reactions that occur in this type of battery when it is being recharged.

Tip: Remember, for Q2 and Q3 the first thing you need to do is to work out which half-reaction is going forwards (reduction) and which is going backwards (oxidation).

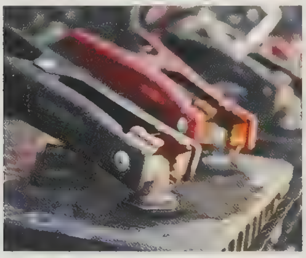


Figure 3: *Lead-acid car batteries being recharged.*

Tip: When a rechargeable battery is being used, the forward reaction will be taking place and $E^{\ominus}_{cell}$ will be positive. When the battery is being recharged, the reverse reaction will be taking place and $E^{\ominus}_{cell}$ will be negative.

Practice Questions — Fact Recall

Q1 What is the common name for an energy storage cell?

Q2 Give the equation you would use to calculate the cell potential of an energy storage cell.

Q3 Why can some energy storage cells be recharged?

8. Fuel Cells

Fuel cells are really handy — they can generate electricity without producing too much pollution and they're more efficient than petrol engines.

Learning Objective:

- Be able to explain that a fuel cell uses the energy from the reaction of a fuel with oxygen to create a voltage.
- Be able to explain the changes that take place at each electrode in a fuel cell.

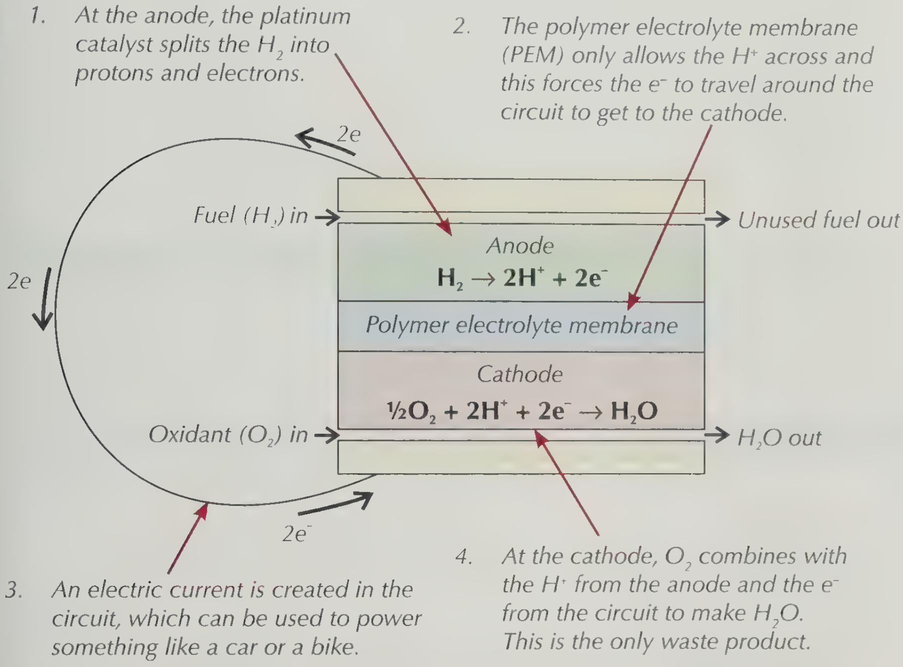
Specification Reference 5.2.3

What are fuel cells

A **fuel cell** produces electricity by reacting a fuel with oxygen. The fuel is oxidised at the anode and the oxidant is reduced at the cathode.

Hydrogen-oxygen fuel cells

In a hydrogen-oxygen fuel cell, the fuel used is hydrogen. Hydrogen-oxygen fuel cells can operate in acidic or alkaline conditions. Figure 1 shows how an acidic hydrogen-oxygen fuel cell works:


2e
Fuel (H_2) in
Unused fuel out
2e
Anode
$H_2 \rightarrow 2H^+ + 2e^-$
Polymer electrolyte membrane
Cathode
$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$
Oxidant (O_2) in
H_2O out
$2e^-$

1. *At the anode, the platinum catalyst splits the H_2 into protons and electrons.*
2. *The polymer electrolyte membrane (PEM) only allows the H^+ across and this forces the e^- to travel around the circuit to get to the cathode.*
3. *An electric current is created in the circuit, which can be used to power something like a car or a bike.*
4. *At the cathode, O_2 combines with the H^+ from the anode and the e^- from the circuit to make H_2O. This is the only waste product.*

Figure 1: *An acidic hydrogen-oxygen fuel cell*

The fuel cell shown in Figure 1 involves H^+ ions crossing the electrolyte in order to balance the half-reactions at each electrode. This makes it an acidic fuel cell. The overall redox reaction for this cell, found by combining the half-equations, is:

$$\frac{1}{2}O_2 + H_2 \rightarrow H_2O$$

You can also make alkaline hydrogen-oxygen fuel cells. The set-up is very similar to the cell in Figure 1, except that the electrolyte is alkaline and the polymer electrolyte membrane only allows OH^- ions across. In an alkaline hydrogen-oxygen fuel cell, the half-equations are:

$$\text{Anode: } H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$$
$$\text{Cathode: } \frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^-$$

But the overall redox reaction happening in the alkaline fuel cell is the same as the overall reaction for the acidic fuel cell:

$$\frac{1}{2}O_2 + H_2 \rightarrow H_2O$$

Tip: There are lots of advantages of using a fuel cell, rather than a standard petrol engine. For example, fuel cells are more efficient at producing energy because energy is wasted during combustion as heat. They also produce a lot less pollution (such as CO_2). For hydrogen fuel cells, the only waste product is water.

You can calculate the cell potential of a fuel cell just like you would for any other cell.

Example — **Maths Skills**

$H_2 \rightleftharpoons 2H^+ + 2e^-$ $E^\ominus = 0.00$ V $\frac{1}{2}O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O$ $E^\ominus = +1.23$ V

The $H_2/2H^+$ half-cell has the more negative electrode potential, so this half reaction will go in the direction of oxidation. The O_2/O^{2-} half-cell has the more positive electrode potential and so will go in the direction of reduction.

$$E^\ominus_{\text{cell}} = E^\ominus_{\text{reduced}} - E^\ominus_{\text{oxidised}} = 1.23 - (0.00) = +1.23 \text{ V}$$

Tip: This question might look a bit scary, since it's a slightly different type of fuel cell to the one on the previous page, but just remember — the fuel will be oxidised at the anode and the oxidant will be reduced at the cathode.

Practice Question — Application

Q1 The following reactions take place in a methanol fuel cell:

$CH_3OH + H_2O \rightleftharpoons CO_2 + 6H^+ + 6e^-$ $E^\ominus = +0.046$ V

$1\frac{1}{2}O_2 + 6H^+ + 6e^- \rightleftharpoons 3H_2O$ $E^\ominus = +1.23$ V

a) Write an overall equation for the reaction in the methanol fuel cell.

b) Which reaction occurs at: i) the cathode? ii) the anode?

c) What is the cell potential of the methanol fuel cell?

Practice Questions — Fact Recall

Q1 How does a fuel cell produce electricity?

Q2 Describe how an acidic hydrogen-oxygen fuel cell works.

Section Summary

Make sure you know...

- The meaning of the terms redox reaction, half-reaction, oxidising agent and reducing agent.
- What half-equations are and how to use them to write full equations for redox reactions.
- That oxidation numbers change as part of a redox reaction.
- What oxidation numbers are and how to use them to write redox equations.
- How to carry out redox titrations involving the manganate(VII) ion (MnO_4^-).
- How to carry out iodine-sodium thiosulfate ($I_2/S_2O_3^{2-}$) redox titrations.
- How to perform calculations based on experimental redox titration results.
- What electrochemical cells are and how to draw diagrams of them.
- How to set up an electrochemical cell and use it to measure voltages.
- What factors affect the electrode potential of a half-cell.
- How to use a standard hydrogen electrode to measure the standard electrode potential of a half-cell.
- What an electrochemical series is.
- How to calculate a standard cell potential using two standard electrode potentials.
- How to use standard electrode potentials to predict the direction of reactions.
- Why these reaction predictions are sometimes wrong.
- What energy storage cells are.
- How to calculate the voltages that energy storage cells produce (their cell potentials).
- The risks and benefits associated with using electrochemical cells.
- What fuel cells are and how they work.

Exam-style Questions

1 The table below shows a short electrochemical series:

Half-reaction	$E^\ominus$ (V)
$Al^{3+}_{(aq)} + 3e^- \rightleftharpoons Al_{(s)}$	–1.66
$Zn^{2+}_{(aq)} + 2e^- \rightleftharpoons Zn_{(s)}$	–0.76
$Ni^{2+}_{(aq)} + 2e^- \rightleftharpoons Ni_{(s)}$	–0.25
$Cu^{2+}_{(aq)} + 2e^- \rightleftharpoons Cu_{(s)}$	+0.34
$Fe^{3+}_{(aq)} + e^- \rightleftharpoons Fe^{2+}_{(aq)}$	+0.77

Using the information in the table, determine which of the following reactions is not feasible.

A $Zn_{(s)} + 2Fe^{3+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + 2Fe^{2+}_{(aq)}$

B $2Al_{(s)} + 3Ni^{2+}_{(aq)} \rightarrow 2Al^{3+}_{(aq)} + 3Ni_{(s)}$

C $Ni_{(s)} + Cu^{2+}_{(aq)} \rightarrow Ni^{2+}_{(aq)} + Cu_{(s)}$

D $3Zn_{(s)} + 2Al^{3+}_{(aq)} \rightarrow 3Zn^{2+}_{(aq)} + 2Al_{(s)}$

(1 mark)

2 Magnesium metal will react with iron(II) sulfate to give magnesium sulfate and metallic iron:

$$Mg_{(s)} + FeSO_{4\,(aq)} \rightarrow MgSO_{4\,(aq)} + Fe_{(s)}$$

Which of the following elements is reduced during this reaction?

A Mg

B Fe

C S

D O

(1 mark)

3 As part of a redox titration, a solution of a colourless reducing agent containing Fe(II) ions was placed in a conical flask. It was titrated with a solution of manganate(VII) ions. What colour change would you expect to see at the endpoint of this titration?

- **A** The solution in the conical flask changes from colourless to orange.
- **B** The solution in the conical flask changes from colourless to purple.
- **C** The solution in the conical flask changes from purple to colourless.
- **D** The solution in the conical flask changes from brown to colourless.

(1 mark)

4 Nickel-zinc cells are a type of rechargeable battery used in digital cameras. The half-equations for the reactions that occur in a nickel-zinc cell are shown below:

$NiOOH_{(s)} + H_2O_{(l)} + e^- \rightleftharpoons Ni(OH)_{2(s)} + OH^-_{(aq)}$ $E^\circ = ?\,V$

$Zn(OH)_{2(s)} + 2e^- \rightleftharpoons Zn_{(s)} + 2OH^-_{(aq)}$ $E^\circ = -1.25\,V$

When the cell discharges, the Zn/$Zn(OH)_2$ half-reaction goes in the oxidation direction.

(a) Give the equation for the overall reaction occurring in this cell as it discharges.

(2 marks)

(b) The standard cell potential for this cell is +1.73 V. Calculate the standard electrode potential of the NiOOH/$Ni(OH)_2$ half-reaction.

(2 marks)

5 Lithium-thionyl chloride cells are a type of energy storage cell (battery) used in medical applications. The half-equations for the two half-cells that make up this type of cell are shown below:

$Li^+_{(aq)} + e^- \rightleftharpoons Li_{(s)}$ $E^\circ = -3.04\,V$

$2SOCl_{2(aq)} + 4Li^+_{(aq)} + 4e^- \rightarrow 4LiCl_{(s)} + S_{(s)} + SO_{2(g)}$ $E^\circ = +0.47\,V$

(a) Give the equation for the overall reaction occurring in this cell as it discharges.

(2 marks)

(b) Calculate the cell potential for the reaction as the cell discharges.

(1 mark)

(c) Give one advantage and one disadvantage of using energy storage cells.

(2 marks)

6 The table below shows a short electrochemical series:

Half-reaction	$E^\ominus$ (V)
$Mg^{2+}_{(aq)} + 2e^- \rightleftharpoons Mg_{(s)}$	–2.38
$V^{2+}_{(aq)} + 2e^- \rightleftharpoons V_{(s)}$	–1.18
$V^{3+}_{(aq)} + e^- \rightleftharpoons V^{2+}_{(aq)}$	–0.26
$Sn^{4+}_{(aq)} + 2e^- \rightleftharpoons Sn^{2+}_{(aq)}$	+0.15
$VO^{2+}_{(aq)} + 2H^+_{(aq)} + e^- \rightleftharpoons V^{3+}_{(aq)} + H_2O_{(l)}$	+0.34
$Fe^{3+}_{(aq)} + e^- \rightleftharpoons Fe^{2+}_{(aq)}$	+0.77
$VO_2{}^+{}_{(aq)} + 2H^+_{(aq)} + e^- \rightleftharpoons VO^{2+}_{(aq)} + H_2O_{(l)}$	+1.00

(a) (i) Using the information in the table, predict what reactions, if any, will occur when aqueous Sn^{2+} ions are mixed with an acidified solution of $VO_2{}^+$ ions. Explain your answer.

(4 marks)

(ii) Suggest two reasons why your predictions may be incorrect.

(2 marks)

(b) An electrochemical cell can be made by connecting an Mg^{2+}/Mg half-cell to an Fe^{2+}/Fe^{3+} half-cell.

(i) Draw a diagram to show how this cell could be set up in a laboratory.

(3 marks)

(ii) Calculate the cell potential (e.m.f.) of this cell.

(1 mark)

(iii) Write an equation for the overall reaction occurring in this cell.

(2 marks)

(c) Standard electrode potentials are measured relative to the standard hydrogen electrode.

(i) Explain what is meant by 'standard conditions'.

(3 marks)

(ii) The electrode itself is made of platinum foil.
Suggest why platinum is a suitable metal to use for this purpose.

(1 mark)

(d) When a standard hydrogen electrode was connected to an Ag^+/Ag half-cell, the reading on the voltmeter was +0.80 V.
What is the standard electrode potential for the reaction $Ag^+_{(aq)} + e^- \rightleftharpoons Ag_{(s)}$?

(1 mark)

7 Lithium-ion batteries are a type of rechargeable battery commonly used in mobile phones. The half-equations for the reactions that occur in a lithium-ion battery as it discharges are shown below:

$$Li^{+}_{(aq)} + CoO_{2(s)} + e^{-} \rightleftharpoons Li^{+}[CoO_2]^{-}_{(s)}$$

$$Li_{(s)} \rightleftharpoons Li^{+}_{(aq)} + e^{-}$$

(a) Give the overall equation for the reaction occurring in this cell as it is being recharged.

(1 mark)

(b) Explain why rechargeable batteries can be recharged.

(1 mark)

8 Brass is an alloy of copper and zinc. The percentage composition of copper in brass can be determined using an iodine-sodium thiosulfate titration because the copper ion (Cu^{2+}) is an oxidising agent.

1.00 g of brass was dissolved in acid and added to an excess of acidified potassium iodide solution. The equation for the reaction that took place is shown below.

$$2Cu^{2+}_{(aq)} + 4I^{-}_{(aq)} \rightarrow 2CuI_{(aq)} + I_{2\,(aq)}$$

This solution was then titrated against sodium thiosulfate.
The equation for this reaction is shown below.

$$I_{2\,(aq)} + 2S_2O_3^{2-}{}_{(aq)} \rightarrow 2I^{-}_{(aq)} + S_4O_6^{2-}{}_{(aq)}$$

It took 23.6 cm^3 of 0.500 mol dm^{-3} sodium thiosulfate solution to reach the end point of the reaction.

(a) Describe how you would perform the titration part of the experiment.

(5 marks)

(b) Use the information given above to calculate the number of moles of Cu^{2+} ions present in the brass solution.

(3 marks)

(c) Work out the percentage composition by mass of copper in the 1 g sample of brass.

(2 marks)

1. Transition Elements

Some of the most precious materials in the world are transition elements. Transition elements are responsible for some pretty interesting and important chemistry, which is why there's a whole section of this book devoted to them.

The d-block

The **d-block** is the block of elements in the middle of the periodic table. Most of the elements in the d-block are **transition elements** (or transition metals). You only need to know about the ones in the first row of the d-block (Period 4). These are the elements from titanium to copper — see Figure 1.

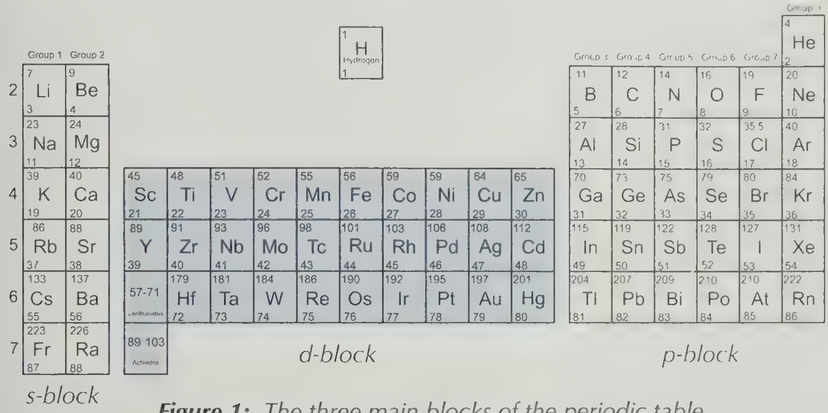

Group 1
Group 2
Group 3
Group 4
Group 5
Group 6
Group 7
Group 0
H Hydrogen
2 Li Be
3 Na Mg
4 K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
5 Rb Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd In Sn Sb Te I Xe
6 Cs Ba 57-71 Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po At Rn
7 Fr Ra 89-103
B C N O F Ne
Al Si P S Cl Ar
He
s-block
d-block
p-block

***Figure 1:** The three main blocks of the periodic table. The transition elements are in the d-block.*

What is a transition element?

Here's the definition of a transition element:

> A transition element is a d-block element that can form at least one stable ion with a partially filled d-sub-shell.

A **d-sub-shell** can take ten electrons. So transition elements form at least one ion with between one and nine electrons in the d-sub-shell. All the Period 4 d-block elements are transition elements apart from scandium and zinc (see page 415).

Electron configurations

The electron configurations of elements can be figured out by following a few simple rules:

- Electrons fill up the lowest energy **sub-shells** first.
- Electrons fill **orbitals** singly before they start sharing.

The transition metals generally follow the same rules — see Figure 3. The 4s sub-shell usually fills up first because it has lower energy than the 3d sub-shell. Once the 4s sub-shell is full, the 3d sub-shell starts to fill up. The 3d orbitals are occupied singly at first. They only double up when they have to. But, there are a couple of exceptions...

Learning Objectives:

- Be able to describe the elements Ti–Cu as transition elements, i.e. d-block elements that have an ion with an incomplete d-sub-shell.
- Be able to deduce the electron configuration of atoms and ions of the d-block elements of Period 4 (Sc–Zn), given the atomic number and charge.

Specification Reference 5.3.1

***Figure 2:** A variety of transition metals.*

Tip: Electron orbitals and electron configurations were covered in Module 2: Section 4, so if you've forgotten what they are have a quick skim over pages 106-109.

Tip: Sub-shells are made up of orbitals — for example, s-sub-shells contain one orbital, p-sub-shells contain three orbitals and d-sub-shells contain five orbitals. Each orbital can hold two electrons.

- Chromium prefers to have one electron in each orbital of the 3d sub-shell and just one in the 4s sub-shell — this gives it more stability.
- Copper prefers to have a full 3d sub-shell and just one electron in the 4s sub-shell — it's more stable that way.

Tip: The electron configurations of all the Period 4 transition metals start in the same way — $1s^2 2s^2 2p^6 3s^2 3p^6$. This is the same as the electron configuration of the element argon, so [Ar] is often used as a short way of writing it.

		3d					*4s*	
Ti	[Ar]	↑	↑				↑↓	[Ar] $3d^2 4s^2$
V	[Ar]	↑	↑	↑			↑↓	[Ar] $3d^3 4s^2$
Cr	[Ar]	↑	↑	↑	↑	↑	↑	[Ar] $3d^5 4s^1$
Mn	[Ar]	↑	↑	↑	↑	↑	↑↓	[Ar] $3d^5 4s^2$
Fe	[Ar]	↑↓	↑	↑	↑	↑	↑↓	[Ar] $3d^6 4s^2$
Co	[Ar]	↑↓	↑↓	↑	↑	↑	↑↓	[Ar] $3d^7 4s^2$
Ni	[Ar]	↑↓	↑↓	↑↓	↑	↑	↑↓	[Ar] $3d^8 4s^2$
Cu	[Ar]	↑↓	↑↓	↑↓	↑↓	↑↓	↑	[Ar] $3d^{10} 4s^1$

Figure 3: *The electron configurations of the Period 4 d-block transition metals.*

Transition metal ions

Transition metal atoms form positive ions. When this happens, the s electrons are removed first, then the d electrons.

Example

Iron forms Fe^{2+} ions and Fe^{3+} ions.

When it forms 2+ ions, it loses both its 4s electrons:

$$Fe = [Ar]3d^6 4s^2 \rightarrow Fe^{2+} = [Ar]3d^6$$

Only once the 4s electrons are removed can a 3d electron be removed.

$$\text{E.g. } Fe^{2+} = [Ar]3d^6 \rightarrow Fe^{3+} = [Ar]3d^5$$

Exam Tip
The atomic number in the periodic table tells you how many electrons each atom has — you should be able to work the electron configuration out from there.

You might be asked to write the electron configuration of a transition metal ion in the exam. To do this, just follow these steps:

- Write down the electron configuration of the atom.
- Work out how many electrons have been removed to make the ion by looking at the charge on the ion.
- Remove that number of electrons from the electron configuration, taking them out of the s-orbital first and then the d-orbitals.

Example

Write out the electron configuration of Mn^{2+} ions.

- The electron configuration of Mn atoms is $[Ar]3d^5 4s^2$.
- Two electrons are removed to convert Mn atoms into Mn^{2+} ions.
- Removing the electrons starting from the s-orbitals gives $[Ar]3d^5 4s^0$.
- So the electron configuration of Mn^{2+} ions is $[Ar]3d^5$.

Scandium and zinc

Sc and Zn aren't transition elements as their stable ions don't have partially filled d-sub-shells.

Scandium only forms one ion, Sc^{3+}, which has an empty d-sub-shell. Scandium has the electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^1 4s^2$, so when it loses three electrons to form Sc^{3+}, it ends up with the electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6$.

Zinc only forms one ion, Zn^{2+}, which has a full d-sub-shell. Zinc has the electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2$. When it forms Zn^{2+} it loses two electrons, both from the 4s sub-shell. This means it keeps its full 3d sub-shell and becomes $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$.

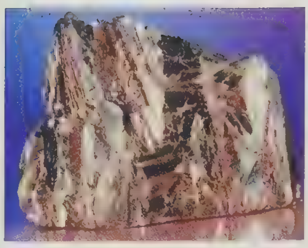


Figure 4: *A lump of zinc.*

Practice Questions — Application

Q1 Write out the electron configurations for the following transition metal elements:

a) V b) Co c) Mn d) Ni

Q2 Write out the electron configurations for the following transition metal ions:

a) V^{3+} b) Co^{2+} c) Mn^{2+} d) Ni^{2+}

e) Cr^{2+} f) Ti^{3+} g) Ti^{4+}

Q3 Using electron configurations, explain why zinc is not a transition element, despite being in the d-block of the periodic table.

Exam Tip

If you're asked for a full electron configuration you need to write it all out starting from $1s^2$ — don't use [Ar].

Practice Questions — Fact Recall

Q1 Where in the periodic table are transition elements found?

Q2 What is the definition of a transition element?

Q3 How many electrons can a d-sub-shell hold?

Q4 Give two rules that are usually followed when working out electron configurations.

Q5 a) Explain why chromium has the electron configuration $[Ar]3d^5 4s^1$ and not $[Ar]3d^4 4s^2$ as you would expect.

b) Explain why copper has the electron configuration $[Ar]3d^{10} 4s^1$ and not $[Ar]3d^9 4s^2$ as you would expect.

Exam Tip

Chromium and copper have slightly odd electron configurations (see previous page). I'm afraid there's no easy way to work them out in the exam — you'll just have to learn 'em...

2. Transition Element Properties

The chemical properties of transition metals make them great for things like indicators, colouring agents, catalysts and even drugs. But before you can learn about these fascinating applications you have to learn the basics...

Learning Objectives:

- Be able to illustrate the formation of coloured transition metal ions, using at least two examples.
- Be able to illustrate, using at least two examples, the catalytic behaviour of the transition elements and their compounds and their importance in the manufacture of chemicals by industry.
- Be able to illustrate the existence of more than one oxidation state for each transition element in its compounds, using at least two examples.

Specification Reference 5.3.1

Chemical properties

The transition metals have a few special chemical properties that you need to know about:

- They can form **complex ions** — see pages 418-420.
  E.g. iron forms a complex ion with water — $[Fe(H_2O)_6]^{2+}$.
- They form coloured ions — see below.
  E.g. $Fe^{2+}_{(aq)}$ ions are pale green and $Fe^{3+}_{(aq)}$ ions are yellow.
- They're good **catalysts** — see next page.
  E.g. nickel is the catalyst used to harden margarine.
- They can exist in variable **oxidation states** — see below.
  E.g. iron can exist in the +2 oxidation state as Fe^{2+} ions and in the +3 oxidation state as Fe^{3+} ions.

Oxidation states and coloured ions

Some common coloured ions and oxidation states are shown below. The colours refer to the aqueous ions.

Element	Ion	Oxidation state	Colour
Ti	Ti^{2+}	+2	violet
	Ti^{3+}	+3	purple
V	V^{2+}	+2	violet
	V^{3+}	+3	green
	VO^{2+}	+4	blue
	VO_2^{+}	+5	yellow
Cr	Cr^{3+}	+3	pale purple (but usually looks green)
	$Cr_2O_7^{2-}$	+6	orange
Mn	Mn^{2+}	+2	very pale pink/ colourless
	MnO_4^{2-}	+6	green
	MnO_4^{-}	+7	purple
Fe	Fe^{2+}	+2	pale green
	Fe^{3+}	+3	yellow
Co	Co^{2+}	+2	pink
Ni	Ni^{2+}	+2	green
Cu	Cu^{2+}	+2	pale blue

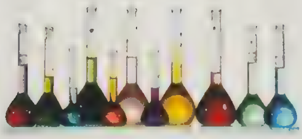


***Figure 1:** The different colours of the aqueous transition metal ions.*

Tip: See page 386 for more on oxidation states and how to find them.

These elements show variable oxidation states because the energy levels of the 4s and the 3d sub-shells are very close to one another. So different numbers of electrons can be gained or lost using fairly similar amounts of energy.

Transition metal catalysts

Transition elements and their compounds make good **catalysts** because they can change oxidation states by gaining or losing electrons within their d orbitals. This means they can transfer electrons to speed up reactions. Transition metals are also good at adsorbing substances onto their surfaces to lower the activation energy of reactions.

Examples

- Iron is the catalyst used in the Haber process to produce ammonia.

$$N_{2(g)} + 3H_{2(g)} \xrightarrow{Fe_{(s)}} 2NH_{3(g)}$$

- Copper(II) sulfate ($CuSO_4$) is the catalyst used in the reaction of zinc and acids.

$$Zn_{(s)} + H_2SO_{4(aq)} \xrightarrow{CuSO_{4(s)}} ZnSO_{4(aq)} + H_{2(g)}$$

- Manganese(IV) oxide (MnO_2) is the catalyst used in the decomposition of hydrogen peroxide.

$$2H_2O_{2(aq)} \xrightarrow{MnO_{2(s)}} 2H_2O_{(l)} + O_{2(g)}$$

Tip: Using transition element catalysts can pose health risks as many of the metals and their compounds are toxic. For example, long term exposure to copper can damage the liver and kidneys, and exposure to manganese can cause psychiatric problems.

Catalysts are good for industry and for the environment as they allow reactions to happen faster and at lower temperatures and pressures, reducing energy usage.

The partially filled d-sub-shell

It's the partially filled d-sub-shell that causes the special chemical properties of transition metals. d-block elements without a partially filled d-sub-shell don't have these properties.

Example

Scandium and zinc don't form ions with partially filled d-sub-shells. As a result they don't have the same chemical properties as transition metals.

For example, they can't form complex ions, they don't form coloured ions, they can't exist in variable oxidation states and they don't catalyse any reactions.

Tip: There's more on scandium and zinc on page 415.

Practice Questions — Fact Recall

Q1 Transition elements have variable oxidation states.
State two other chemical properties of transition elements.

Q2 Match the transition metal ions (**A**–**D**) with the colour they'd be in solution (**1**–**4**).

A Fe^{3+}

B Mn^{2+}

C MnO_4^-

D Cu^{2+}

1 pale blue

2 purple

3 yellow

4 very pale pink

Q3 Name the catalyst used in the Haber process.

3. Complex Ions

The ability to form complex ions is an important property of transition metals. You probably haven't come across complex ions before, but the next few pages should tell you everything you need to know.

Learning Objectives:

- Be able to use and explain the term ligand in terms of coordinate (dative covalent) bonding to a metal ion or metal.
- Be able use the terms complex ion and coordination number.
- Be able to explain and use the term bidentate ligand (e.g. $NH_2CH_2CH_2NH_2$, 'en').
- Be able to give examples of complexes with six-fold coordination with an octahedral shape.
- Be able to give examples of complexes with four-fold coordination with a planar or tetrahedral shape.

Specification Reference 5.3.1

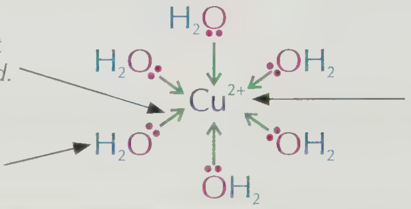
What are complex ions?

A **complex ion** is a metal ion surrounded by coordinately bonded **ligands**.
A **coordinate bond** (or dative covalent bond) is a covalent bond in which both electrons in the shared pair come from the same atom, ion or molecule.
In a complex ion, they come from the ligands. So, a ligand is an atom, ion or molecule that donates a pair of electrons to a central metal ion.

Example

$[Cu(H_2O)_6]^{2+}$

The central metal ion is a Cu^{2+} ion and water molecules are acting as ligands. There are six water molecules, each forming a coordinate bond with the Cu^{2+} ion:



Arrows represent a coordinate bond.

Water molecules act as ligands.

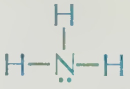
Central transition metal ion.

The different types of ligand

A ligand must have at least one lone pair of electrons, or it won't have anything to use to form a coordinate bond. But, different ligands can have different numbers of lone pairs and can form different numbers of coordinate bonds. Ligands that can only form one coordinate bond are called **monodentate**.

Examples

Here are some examples of monodentate ligands:



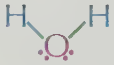
ammonia

$:Cl^-$

chloride ions

$:CN^-$

cyanide ions



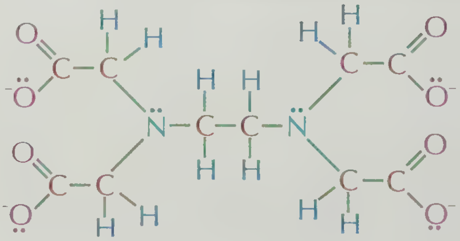
water

Ammonia only has one lone pair of electrons to donate to form a coordinate bond. Water has two lone pairs of electrons but because they are so close together, it can only form one coordinate bond at a time. Chloride ions and cyanide ions can also only form one coordinate bond with a metal ion.

Ligands that can form more than one coordinate bond are called **multidentate**.

Example

$EDTA^{4-}$ is a multidentate ligand:

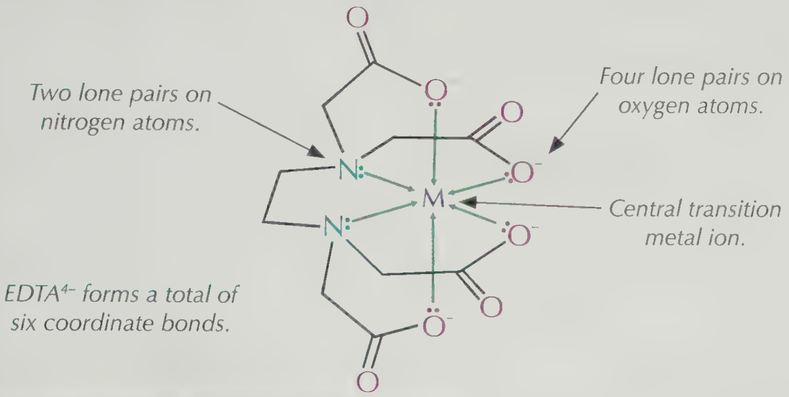


Tip: Charged complex ions are always written in square brackets and the charge is put to the top right of the square brackets, e.g. $[Cu(H_2O)_6]^{2+}$. Uncharged complex ions can be written with or without the brackets.

Tip: Chloride ions and cyanide ions both have more than one lone pair of electrons, but they are only able to donate one lone pair to a central metal ion to form a coordinate bond — so they are both monodentate ligands.

Tip: EDTA stands for ethylenediaminetetra-acetic acid.

$EDTA^{4-}$ has six lone pairs (two on nitrogen atoms and four on oxygen atoms) so it can form six coordinate bonds with a metal ion.


Two lone pairs on nitrogen atoms.
Four lone pairs on oxygen atoms.
Central transition metal ion.
$EDTA^{4-}$ forms a total of six coordinate bonds.
M
N
O

Tip: $EDTA^{4-}$ is hexadentate — hexa meaning six.

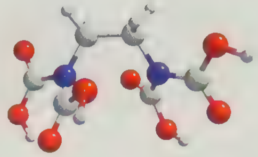


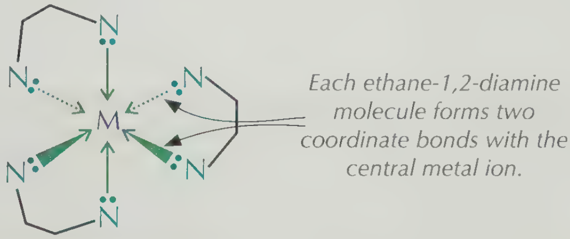
Figure 1: *Molecular model of EDTA.*

Tip: Don't worry — you won't be asked to draw out the structure of $EDTA^{4-}$ in the exam.

Multidentate ligands that can form two coordinate bonds are called **bidentate**.

Example

Ethane-1,2-diamine ($\ddot{N}H_2CH_2CH_2\ddot{N}H_2$) is a bidentate ligand. It has two amine groups, each of which has a lone pair of electrons that it can donate to form a coordinate bond. In complex ions, each ethane-1,2-diamine molecule forms two coordinate bonds with the metal ion. In the complex ion below, there are three ethane-1,2-diamine molecules forming six coordinate bonds:


Each ethane-1,2-diamine molecule forms two coordinate bonds with the central metal ion.
M
N

Tip: Ethane-1,2-diamine ligands can be abbreviated to 'en'. For example, $[Cu(en)_3]^{2+}$.

Shapes of complex ions

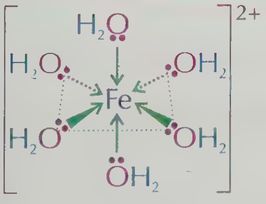
The shape of a complex ion depends on its **coordination number**. This is the number of coordinate bonds that are formed with the central metal ion. The usual coordination numbers are 6 and 4. If the ligands are small, like H_2O, CN^- or NH_3, 6 can fit around the central metal ion. But if the ligands are larger, like Cl^-, only 4 can fit around the central metal ion.

Tip: A complex ion's coordination number depends on the number of bonds formed with the ligands — not the number of ligands. So, a complex ion that has 3 bidentate ligands will have a coordination number of 6 (3 ligands each forming 2 bonds).

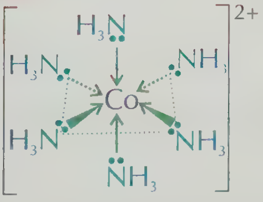
Six coordinate bonds

Complex ions that contain six coordinate bonds have an octahedral shape. In an octahedral structure all of the bond angles are 90°.

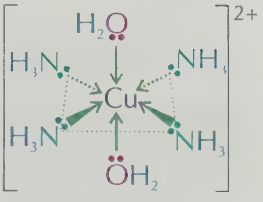
Examples **Maths Skills**



$[Fe(H_2O)_6]^{2+}_{(aq)}$



$[Co(NH_3)_6]^{2+}_{(aq)}$


H_2O
H_3N
NH_3
OH_2
Cu
2+

$[Cu(NH_3)_4(H_2O)_2]^{2+}_{(aq)}$

Tip: In complex ions, the ligands don't all have to be the same — you can have mixtures of different ligands in the same complex.

Many octahedral complex ions are hexaaqua complexes. This means there are six water ligands around the central ion.

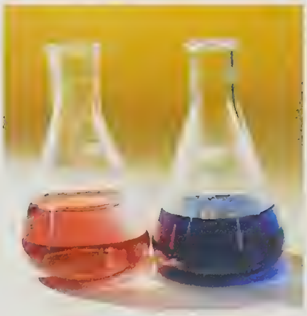


Figure 2: *The flask on the left shows the pink colour of hexaaquacobalt(II) ions. The flask on the right shows the blue colour of cobalt(II) ions complexed as $[CoCl_4]^{2-}$.*

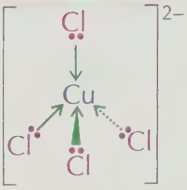
The different types of bond arrow show that the complex is 3D. The wedge-shaped arrows represent bonds coming towards you and the dashed arrows represent bonds sticking out behind the molecule.

Four coordinate bonds

Complex ions with four coordinate bonds usually have a tetrahedral shape and 109.5° bond angles.

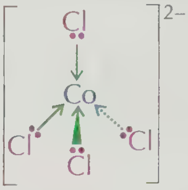
Examples — **Maths Skills**

$[CuCl_4]^{2-}$



(yellow)

$[CoCl_4]^{2-}$



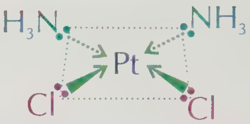
(blue)

But in a few complexes, four coordinate bonds form a square planar shape. All of the bond angles in a square planar structure are 90°.

Tip: Cisplatin is used as an anti-cancer drug. See page 422 for more information on this.

Example — **Maths Skills**

Cisplatin ($Pt(NH_3)_2Cl_2$) (see page 421) has a square planar shape:



Practice Questions — Application

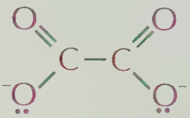
Tip: Remember, 'en' stands for one ethane-1,2-diamine ligand.

Q1 Give the shapes of the following complex ions and draw them:

a) $[CuF_6]^{4-}$ b) $[Fe(OH)_2(H_2O)_4]$ c) $[Fe(en)_3]^{3+}$

Q2 What is the coordination number of the transition metal in each of the complex ions in Q1?

Q3 $C_2O_4^{2-}$ is a bidentate ligand. Its structure is shown on the right.



a) Copy the diagram and circle the atoms that could form a coordinate bond with a metal ion.

b) $C_2O_4^{2-}$ forms an octahedral complex with Cr^{3+}. Give the formula of the complex ion formed.

Tip: To work out the overall charge on a complex ion you just add up all the charges of the ions in the complex.

Q4 $[Ni(CN)_4]^{2-}$ is a complex ion. In $[Ni(CN)_4]^{2-}$, the carbon from the CN^- ion donates one lone pair to the central Ni atom.

a) It does not have a tetrahedral shape. What shape could it have instead?

b) Draw the structure of $[Ni(CN)_4]^{2-}$.

Practice Questions — Fact Recall

Q1 Define the following terms:

a) Ligand b) Coordinate bond c) Complex ion

Q2 What is a bidentate ligand?

Q3 Give an example of an octahedral complex ion.

4. Isomerism in Complex Ions

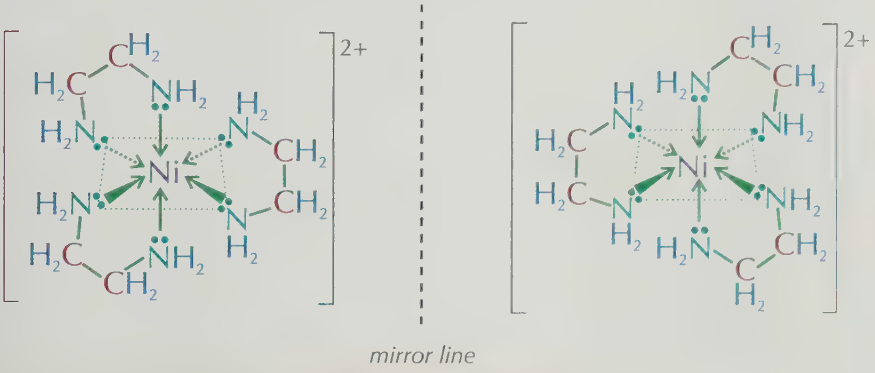
Complex ions can show optical and cis-trans isomerism because the ligands can be arranged in various different ways around the central metal ion.

Optical isomerism in complex ions

Optical isomerism is a type of stereoisomerism. Stereoisomers are molecules with the same structural formula but a different orientation of their bonds in space. For complex ions, optical isomers form when an ion can exist as two non-superimposable mirror images. This happens in octahedral complexes when three bidentate ligands are attached to the central ion. Optical isomers are also known as enantiomers.

Example — **Maths Skills**

When three ethane-1,2-diamine molecules ($H_2NCH_2CH_2NH_2$) use the lone pairs on both nitrogen atoms to coordinately bond with nickel, two optical isomers are formed.



Cis-trans isomerism in complex ions

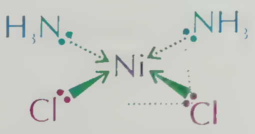
Cis-trans isomerism is another type of stereoisomerism.

Cis-trans isomerism in square planar complex ions

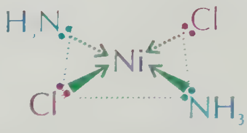
Square planar complex ions that have two pairs of ligands show *cis-trans* isomerism. When two paired ligands are directly opposite each other it's the *trans* isomer and when they're next to each other it's the *cis* isomer.

Example — **Maths Skills**

$NiCl_2(NH_3)_2$ has *cis* and *trans* isomers.



cis-$NiCl_2(NH_3)_2$



trans-$NiCl_2(NH_3)_2$

Cisplatin

Cisplatin is a complex of platinum(II) with two chloride ions and two ammonia molecules in a square planar shape (see Figure 1).

Learning Objectives:

- Be able to describe the types of stereoisomerism shown by complexes, including those associated with bidentate and multidentate ligands.
- Know that complexes can show optical isomerism, e.g. $[Ni(en)_3]^{2+}$.
- Know that complexes can show *cis-trans* isomerism, e.g. $Pt(NH_3)_2Cl_2$.
- Be able to describe the use of cisplatin as an anti-cancer drug and its action by binding to DNA in cancer cells, preventing division.

Specification Reference 5.3.1

Tip: If you're finding it difficult to see that the complexes in the example are mirror images of each other try building their 3D structures using a molecular model kit (or matchsticks and modelling clay).

Exam Tip

If you're asked to draw a complex ion in the exam make sure you use dashed bonds and wedged bonds to show that the structure is 3D — you'll lose marks if you don't.

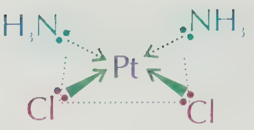


Figure 1: *The structure of cisplatin.*

Tip: If the two chloride ligands were on opposite sides of the complex to each other the molecule would be transplatin. Transplatin has different biological effects to cisplatin.

Cisplatin can be used to treat some types of cancer. Cancer is caused by cells in the body dividing uncontrollably and forming tumours. Cisplatin is active against a variety of cancers, including lung and bladder cancer, because it prevents cancer cells from reproducing.

Before a cell can divide it has to replicate its DNA, which involves unwinding the two strands of the DNA double helix so that they can be copied. Cisplatin easily loses its chloride ligands through a displacement reaction and forms coordinate bonds with nitrogen atoms in the DNA molecule. This prevents the two strands from unwinding. So, the cell can no longer replicate its DNA and it can't divide.

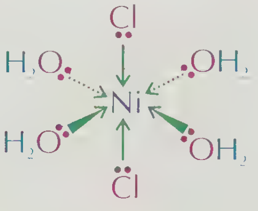
Tip: HOW SCIENCE WORKS The downside is that cisplatin also prevents normal cells from reproducing — including blood and hair cells. This can cause hair loss, and suppress the immune system, which increases the risk of infection. Cisplatin may also cause damage to the kidneys. Scientists always need to weigh up the benefits and risks of new inventions before releasing them for public use. See page 4 for more on decision-making in science.

Cis-trans isomerism in octahedral complex ions

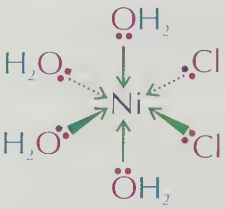
Octahedral complexes with four ligands of one type and two ligands of another type can also exhibit *cis-trans* isomerism. If the two odd ligands are opposite each other you've got the *trans* isomer, if they're next to each other then you've got the *cis* isomer.

Example — Maths Skills

$NiCl_2(H_2O)_4$ has a *trans* and a *cis* isomer.



trans-$NiCl_2(H_2O)_4$



cis-$NiCl_2(H_2O)_4$

Practice Questions — Application

Q1 State what type of stereoisomerism the following complex ions will exhibit:

a) $PtCl_2(H_2O)_2$

b) $[Co(en)_3]^{2+}$

c) $Cu(OH)_2(H_2O)_4$

Q2 Draw the *cis* and *trans* isomers of $NiCl_2(H_2O)_2$.

Tip: If you're asked about the isomerism shown in a complex ion sometimes it helps to draw out the structure of the ion first — then you'll get a better idea of the possible isomers.

Practice Questions — Fact Recall

Q1 Name two types of stereoisomerism that complex ions can exhibit.

Q2 a) Draw the structure of cisplatin.

b) Cisplatin can be used to treat some types of cancer. Explain how cisplatin can work as an anti-cancer drug.

5. Ligand Substitution

Ligands around a central metal ion can switch places with other ligands in ligand substitution reactions.

Ligand substitution reactions

One ligand can be swapped for another ligand — this is **ligand substitution** (or ligand exchange). It pretty much always causes a colour change.

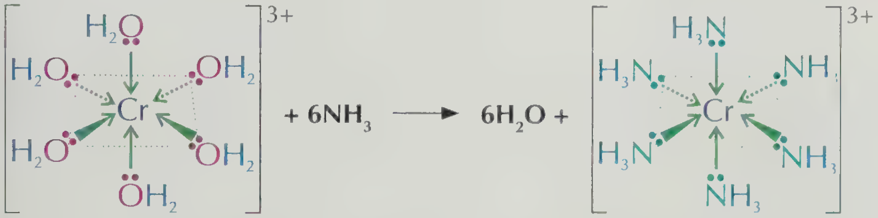
Substitution of similarly sized ligands

If the ligands are of similar size then the coordination number of the complex ion doesn't change, and neither does the shape.

Example

H_2O and NH_3 ligands are similarly sized and are both uncharged. This means that H_2O ligands can be exchanged with NH_3 ligands without any change in coordination number or shape. There will still be a colour change due to the change of ligand.

$$[Cr(H_2O)_6]^{3+}_{(aq)} + 6NH_{3(aq)} \rightarrow 6H_2O_{(l)} + [Cr(NH_3)_6]^{3+}_{(aq)}$$



Coordination number: 6 octahedral, pale purple

(Though, in practice, solutions containing this complex often look green.)

Coordination number: 6 octahedral, purple

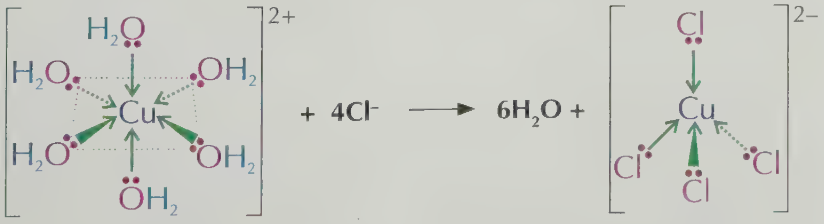
Substitution of different sized ligands

If the ligands are different sizes there's a change of coordination number and a change of shape.

Example

In a copper-aqua complex, the H_2O ligands can be exchanged with Cl^- ligands. You can add Cl^- ions to a solution by adding hydrochloric acid. The shape of the complex changes from octahedral to tetrahedral because fewer of the larger Cl^- ligands can fit around the central metal ion. There is also a colour change during this reaction.

$$[Cu(H_2O)_6]^{2+}_{(aq)} + 4Cl^-_{(aq)} \rightleftharpoons 6H_2O_{(l)} + [CuCl_4]^{2-}_{(aq)}$$



Coordination number: 6 octahedral, pale blue

Coordination number: 4 tetrahedral, yellow-green

Learning Objectives:

- Be able to describe the ligand substitution reaction and the accompanying colour change in the formation of $[Cr(NH_3)_6]^{3+}$ from $[Cr(H_2O)_6]^{3+}$.
- Be able to describe the ligand substitution reactions and the accompanying colour changes in the formation of $[Cu(NH_3)_4(H_2O)_2]^{2+}$ and $[CuCl_4]^{2-}$ from $[Cu(H_2O)_6]^{2+}$.
- Be able to interpret and predict the outcome of unfamiliar ligand substitution reactions.
- Be able to explain the biochemical importance of iron in haemoglobin, including ligand substitution involving O_2 and CO.

Specification Reference 5.3.1

Exam Tip
When you're writing ligand substitution reactions in the exam make sure your equations are balanced.

Tip: Remember — complex ions with a coordination number of four are usually tetrahedral. Complex ions with a coordination number of six are usually octahedral.

Tip: Have a look back at pages 419-420 for a reminder about the shapes of complex ions.

Partial substitution of ligands

Sometimes the substitution is only partial — not all of the six H_2O ligands are substituted.

Example

In a copper-aqua complex, some of the H_2O ligands can be exchanged with NH_3 ligands whilst some H_2O ligands remain where they are.

In this example, four of the H_2O ligands are substituted with NH_3 ligands. The shape of the complex changes from octahedral to elongated octahedral and there is also a colour change.

$$[Cu(H_2O)_6]^{2+}_{(aq)} + 4NH_{3(aq)} \rightarrow 4H_2O_{(l)} + [Cu(NH_3)_4(H_2O)_2]^{2+}_{(aq)}$$

octahedral
pale blue

elongated octahedral
deep blue

Tip: In the example on the right you only get *trans*-$[Cu(NH_3)_4(H_2O)_2]^{2+}$ when an excess of NH_3 is added. Otherwise you get $Cu(OH)_2(H_2O)_4$ (a blue precipitate) instead.

Exam Tip

You could be asked to predict the outcome of unfamiliar reactions in the exam so try to remember that H_2O, NH_3, OH^-, and CN^- ligands are about the same size but Cl^- ions are a lot larger.

Haem and haemoglobin

Haemoglobin is a protein found in blood that helps to transport oxygen around the body. It contains Fe^{2+} ions, which are hexa-coordinated — six lone pairs are donated to them to form six coordinate bonds. Four of the lone pairs come from nitrogen atoms, which form a circle around the Fe^{2+}. This part of the molecule is called haem. The molecule that the four nitrogen atoms are part of is a multidentate ligand called a **porphyrin**. A protein called a globin and either an oxygen or a water molecule also bind to the Fe^{2+} ion to form an octahedral structure — see Figure 2.

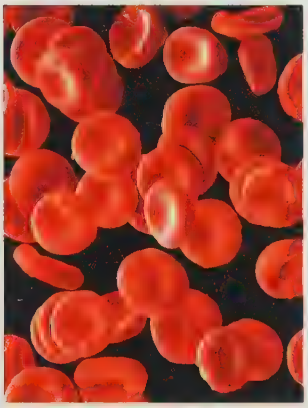


Figure 1: *Red blood cells are packed full of haemoglobin.*

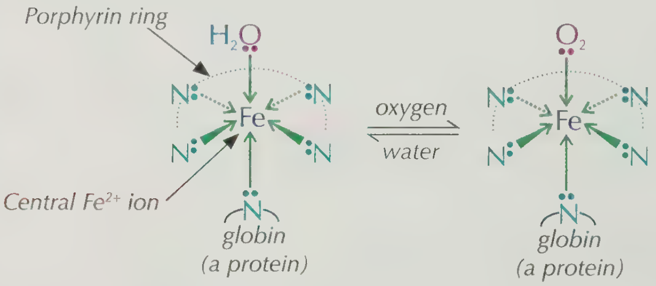


Figure 2: *The structure of haemoglobin when it is bound to oxygen or water.*

In the body, both water and oxygen will bind to the Fe^{2+} ions as ligands, so the complex can transport oxygen to where it's needed, and then swap it for a water molecule. In the lungs, where the oxygen concentration is high, water ligands are substituted for oxygen molecules to form oxyhaemoglobin, which is carried around the body in the blood. When the oxyhaemoglobin gets to a place where oxygen is needed, the oxygen molecules are exchanged for water molecules. The haemoglobin then returns to the lungs and the whole process starts again. The process of oxygen transport is summarised in Figure 4 (on the next page).

Tip: When the Fe^{2+} ion is bound to water the complex is called deoxyhaemoglobin and when it's bound to oxygen it's called oxyhaemoglobin.

Carbon monoxide poisoning

When carbon monoxide is inhaled, the haemoglobin can substitute its water ligands for carbon monoxide ligands, forming carboxyhaemoglobin (Figure 3). This is bad news because carbon monoxide forms a very strong bond with the Fe^{2+} ion and doesn't readily exchange with oxygen or water ligands, meaning the haemoglobin can't transport oxygen any more. Carbon monoxide poisoning starves the organs of oxygen — it can cause headaches, dizziness, unconsciousness and even death if it's not treated.

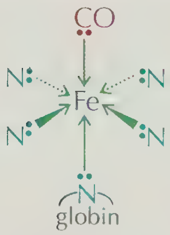


Figure 3: *Carboxyhaemoglobin.*

Summary of the oxygen transport process

Here's an overview of how haemoglobin transports oxygen round the body:

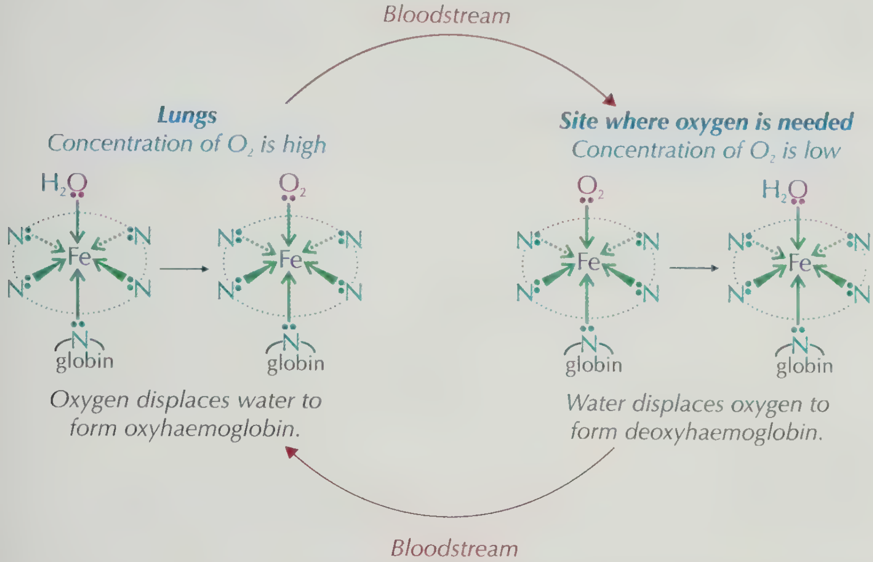

Bloodstream
Lungs
Concentration of O_2 is high
H_2O
O_2
Fe
N
globin
Oxygen displaces water to form oxyhaemoglobin.
Site where oxygen is needed
Concentration of O_2 is low
Water displaces oxygen to form deoxyhaemoglobin.
Bloodstream

Figure 4: *The role of haemoglobin in the transport of oxygen around the body.*

Tip: It's the oxyhaemoglobin in red blood cells that makes them red.

Practice Questions — Application

Q1 The H_2O ligands in $[Fe(H_2O)_6]^{3+}$ can be exchanged for other ligands. Predict the shape of the complex ions formed after the following substitutions:

a) All the H_2O ligands exchanged for OH^- ligands.

b) The six H_2O ligands exchanged for four Cl^- ligands.

Q2 Write an equation for the formation of $[MnCl_4]^{2-}$ from a hexa-aqua manganese(II) ion and chloride ions.

Q3 The metal-aqua ion $[Cu(H_2O)_6]^{2+}$ will undergo a ligand substitution reaction with hydroxide ions to form $[Cu(OH)_4(H_2O)_2]^{2-}$.

a) Write an equation for this reaction.

b) State the shape of $[Cu(OH)_4(H_2O)_2]^{2-}$.

Practice Questions — Fact Recall

Q1 State whether the colour, coordination number and/or the shape of the complex ion changes in the following situations.

a) Ligand exchange of similarly sized ligands.

b) Ligand exchange of differently sized ligands.

Q2 a) What is the role of haemoglobin in the body?

b) Where do the six coordinate bonds come from in haemoglobin?

Q3 Haemoglobin is found in red blood cells.

a) Explain what happens to haemoglobin in the lungs.

b) Explain what happens to haemoglobin at sites where oxygen is needed.

Q4 Explain why carbon monoxide is toxic.

6. Precipitation Reactions

Many transition metals form coloured hydroxide precipitates. Which is pretty handy because it lets us test which transition metal might be in a solution.

Learning Objectives:

- Be able to describe the precipitation reactions, including ionic equations and the accompanying colour changes, of $Cu^{2+}_{(aq)}$, $Fe^{2+}_{(aq)}$, $Fe^{3+}_{(aq)}$, $Mn^{2+}_{(aq)}$ and $Cr^{3+}_{(aq)}$ with aqueous sodium hydroxide and aqueous ammonia (including with excess aqueous sodium hydroxide and aqueous ammonia).
- Be able to interpret and predict the outcome of unfamiliar precipitation reactions.

Specification Reference 5.3.1

Tip: The OH^- ions don't actually replace the water ligands. They just take one H^+ from a water ligand. So the OH^- ion becomes an H_2O molecule and an H_2O ligand becomes an OH^- ligand.

Tip: Remember that a precipitate is a solid formed in a solution.

Transition metal precipitates

When you mix an aqueous solution of transition metal ions with aqueous sodium hydroxide (NaOH) or aqueous ammonia (NH_3) you get a coloured hydroxide **precipitate**.

Notation for precipitation reactions

As you've seen over the last few pages, in aqueous solutions, transition elements take the form $[M(H_2O)_6]^{n+}$. When you're dealing with precipitation reactions they can also be written as $M^{n+}_{(aq)}$ — you can leave out the water ligands. For example, the aqueous copper(II) ion can be written as either $[Cu(H_2O)_6]^{2+}_{(aq)}$ or $Cu^{2+}_{(aq)}$. You can also leave water ligands out of the formula of the precipitate. So the formula of the copper hydroxide precipitate can be written as $Cu(OH)_2(H_2O)_4$ or $Cu(OH)_2$.

Reactions with NaOH and NH_3

In water, sodium hydroxide dissociates into Na^+ and OH^- ions. It's the OH^- ions which react with the transition metal complex.

Example

$$[Fe(H_2O)_6]^{2+}_{(aq)} + 2OH^-_{(aq)} \rightarrow Fe(OH)_2(H_2O)_{4(s)} + 2H_2O_{(l)}$$

pale green — *dark green precipitate*

This can also be written as: $Fe^{2+}_{(aq)} + 2OH^-_{(aq)} \rightarrow Fe(OH)_{2(s)}$

Aqueous transition metal ions will react with ammonia to produce the same hydroxide precipitate as in their reaction with aqueous sodium hydroxide. The ammonia molecules remove H^+ ions from water ligands, creating OH^- ligands.

Example

$$[Fe(H_2O)_6]^{2+}_{(aq)} + 2NH_{3(aq)} \rightarrow Fe(OH)_2(H_2O)_{4(s)} + 2NH_4^+{}_{(aq)}$$

pale green — *dark green precipitate*

Here are the other reactions that you need to know...

Copper(II)

$$[Cu(H_2O)_6]^{2+}_{(aq)} + 2OH^-_{(aq)} \rightarrow Cu(OH)_2(H_2O)_{4(s)} + 2H_2O_{(l)}$$

$$[Cu(H_2O)_6]^{2+}_{(aq)} + 2NH_{3(aq)} \rightarrow Cu(OH)_2(H_2O)_{4(s)} + 2NH_4^+{}_{(aq)}$$

pale blue — *pale blue precipitate*

In excess NH_3, $Cu(OH)_2(H_2O)_{4(s)}$ reacts further to form $[Cu(NH_3)_4(H_2O)_2]^{2+}_{(aq)}$ which is a dark blue colour.

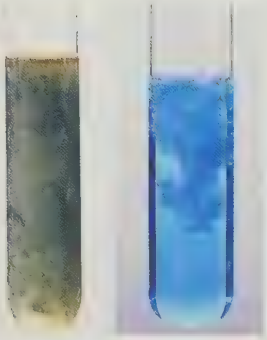


Figure 1: Iron(II) hydroxide (left) and copper(II) hydroxide (right).

Manganese(II)

$[Mn(H_2O)_6]^{2+}_{(aq)} + 2OH^-_{(aq)} \rightarrow Mn(OH)_2(H_2O)_{4(s)} + 2H_2O_{(l)}$

$[Mn(H_2O)_6]^{2+}_{(aq)} + 2NH_{3(aq)} \rightarrow Mn(OH)_2(H_2O)_{4(s)} + 2NH_4{}^+_{(aq)}$

pale pink — *pale brown precipitate*

Iron(III)

$[Fe(H_2O)_6]^{3+}_{(aq)} + 3OH^-_{(aq)} \rightarrow Fe(OH)_3(H_2O)_{3(s)} + 3H_2O_{(l)}$

$[Fe(H_2O)_6]^{3+}_{(aq)} + 3NH_{3(aq)} \rightarrow Fe(OH)_3(H_2O)_{3(s)} + 3NH_4{}^+_{(aq)}$

yellow — *orange-brown precipitate*

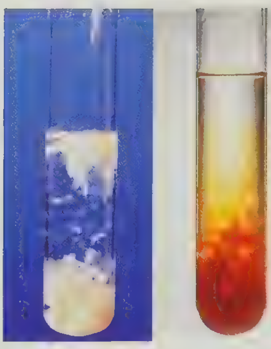


Figure 2: *Manganese(II) hydroxide (left) and iron(III) hydroxide (right).*

Chromium(III)

$[Cr(H_2O)_6]^{3+}_{(aq)} + 3OH^-_{(aq)} \rightarrow Cr(OH)_3(H_2O)_{3(s)} + 3H_2O_{(l)}$

$[Cr(H_2O)_6]^{3+}_{(aq)} + 3NH_{3(aq)} \rightarrow Cr(OH)_3(H_2O)_{3(s)} + 3NH_4{}^+_{(aq)}$

green — *dark green precipitate*

In excess NaOH, $Cr(OH)_3(H_2O)_{3(s)}$ reacts further to form $[Cr(OH)_6]^{3-}_{(s)}$ which is a dark green colour. In excess NH_3, $Cr(OH)_3(H_2O)_{3(s)}$ reacts further to form $[Cr(NH_3)_6]^{3+}_{(aq)}$ which is a purple colour.

Exam Tip

Notice that the metal ions with a 2+ charge form precipitates with two hydroxide ions and the metal ions with a 3+ charge form precipitates with three hydroxide ions — it makes it a bit easier to remember the equations.

Practice Questions — Application

Q1 A scientist has a solution of Fe ions. Describe a test the scientist could use to determine whether the ions are Fe^{2+} ions or Fe^{3+} ions.

Q2 A few drops of aqueous ammonia are added to a pink aqueous cobalt(II) solution. A blue precipitate is formed. Write an equation for the reaction that's likely to have taken place.

Practice Questions — Fact Recall

Q1 Write an equation for the reaction of copper(II) ions with sodium hydroxide solution.

Q2 What would you observe as sodium hydroxide solution is added to a solution of iron(III) ions?

7. Transition Metals and Redox

Learning Objectives:

- Know the redox reactions and accompanying colour changes for the interconversion between Fe^{2+} and Fe^{3+}.
- Know the redox reactions and accompanying colour changes for the interconversion between Cr^{3+} and $Cr_2O_7^{2-}$.
- Know the redox reactions and accompanying colour changes for the reduction of Cu^{2+} to Cu^+ and disproportionation of Cu^+ to Cu^{2+} and Cu.
- Be able to interpret and predict the outcome of unfamiliar redox reactions.

Specification Reference 5.3.1

You learnt all about redox reactions on pages 385-386. In redox reactions, one species gains electrons and is reduced, another loses electrons and is oxidised. Here's a nice topic all about redox reactions involving transition elements.

Transition metal redox reactions

Transition elements can exist in many different **oxidation states**. They can change oxidation state by gaining or losing electrons in redox reactions. This often brings about a colour change.

Interconversion between Fe^{3+} and Fe^{2+}

Iron ions can gain and lose electrons to switch between the Fe^{2+} and Fe^{3+} states when appropriate oxidising and reducing agents are added to their solutions.

The oxidation of Fe^{2+} to Fe^{3+} by Mn(VII) ions in acid solution

Acidified potassium manganate(VII) solution, $KMnO_{4(aq)}$, is used as an oxidising agent. It contains manganate(VII) ions (MnO_4^-), in which manganese has an oxidation state of +7. The manganese(VII) ions are reduced to Mn^{2+} ions and the Fe^{2+} ions are oxidised to Fe^{3+}.

Half equations: $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ *and* $Fe^{2+} \rightarrow Fe^{3+} + e^-$

Five electrons are transferred in the first half-equation and only one is transferred in the second half-equation. So to get the full equation you need to multiply the second half-equation by five, then cancel out the electrons.

So the full equation is: $\mathbf{MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}}$

Tip: The H^+ ions are there because the $KMnO_4$ is acidified.

$Fe^{2+}_{(aq)}$ is pale green and $Fe^{3+}_{(aq)}$ is yellow, so you'll see a colour change from pale green to yellow during this reaction.

The reduction of Fe^{3+} to Fe^{2+} by iodide ions in solution

Iodide solution, $I^-_{(aq)}$, is a reducing agent. The iodide ions have an oxidation state of –1. They can be oxidised to neutral iodine molecules, $I_{2(aq)}$, during a redox reaction with Fe^{3+} ions. The Fe^{3+} ions are reduced.

Half-equations: $2I^- \rightarrow I_2 + 2e^-$ *and* $Fe^{3+} + e^- \rightarrow Fe^{2+}$

Full equation: $\mathbf{2I^- + 2Fe^{3+} \rightarrow 2Fe^{2+} + I_2}$

The reaction mixture starts off as orange-brown and turns brown.

Exam Tip
Don't worry — you won't be expected to memorise and reproduce these full equations in the exams. You could be asked to construct and interpret redox equations from half-equations and oxidation numbers though — so make sure you understand how to do it.

Interconversion between Cr^{3+} and $Cr_2O_7^{2-}$

Chromium ions can gain and lose electrons easily to switch between Cr^{3+} (oxidation state = +3) and $Cr_2O_7^{2-}$ (Cr oxidation state = +6) when appropriate oxidising and reducing agents are added to solutions.

Exam Tip
You will be expected to know the colour changes that take place during these reactions.

The oxidation of Cr^{3+} to dichromate(VI) $Cr_2O_7^{2-}$

There are a couple of steps in this reaction.

Firstly, Cr^{3+} ions in $Cr(OH)_6^{3-}$ are oxidised to CrO_4^{2-} where they have an oxidation state of +6. Hydrogen peroxide solution, $H_2O_{2(aq)}$, is used as the oxidising agent. The oxygen in H_2O_2 is reduced from an oxidation state of –1 to –2 in hydroxide ions, $OH^-_{(aq)}$.

Half-equations: $H_2O_2 + 2e^- \rightarrow 2OH^-$

$2Cr(OH)_6^{3-} + 4OH^- \rightarrow 2CrO_4^{2-} + 8H_2O + 6e^-$

Full equation: $3H_2O_2 + 2Cr(OH)_6^{3-} \rightarrow 2OH^- + 2CrO_4^{2-} + 8H_2O$

dark green *yellow*

In the second step, dilute sulfuric acid is added to the chromate(VI) solution ($CrO_4^{2-}{}_{(aq)}$) to produce a dichromate(VI) solution ($Cr_2O_7^{2-}{}_{(aq)}$).

$$2CrO_4^{2-}{}_{(aq)} + 2H^+_{(aq)} \rightarrow Cr_2O_7^{2-}{}_{(aq)} + H_2O_{(l)}$$

yellow *orange*

Tip: There are a couple of colour changes in the oxidation of Cr^{3+} to $Cr_2O_7^{2-}$. You start with a dark green solution ($Cr(OH)_6^{3-}$) then a yellow one (CrO_4^{2-}) and finally an orange solution ($Cr_2O_7^{2-}$).

The reduction of $Cr_2O_7^{2-}$ to Cr^{3+} by acidified zinc

Acidified zinc, $Zn_{(aq)}$, is a reducing agent. The zinc atoms (oxidation state 0) are oxidised to Zn^{2+} ions (oxidation state +2) in a redox reaction with $Cr_2O_7^{2-}$ ions.

Half-equations: $Zn \rightarrow Zn^{2+} + 2e^-$

$Cr_2O_7^{2-} + 14H^+ + 6e \rightarrow 2Cr^{3+} + 7H_2O$

Full equation: $Cr_2O_7^{2-} + 14H^+ + 3Zn \rightarrow 2Cr^{3+} + 7H_2O + 3Zn^{2+}$

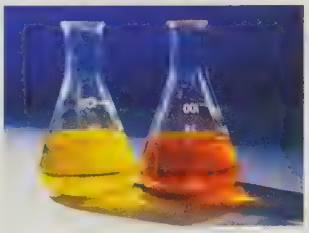


Figure 1: *Left — chromate (CrO_4^{2-}) solution. Right — dichromate ($Cr_2O_7^{2-}$) solution.*

Copper redox reactions

Cu^{2+} ions can be reduced to Cu^+, giving an oxidation state change of +2 to +1.

Example

$Cu^{2+}_{(aq)}$ (pale blue) is reduced to the white precipitate copper(I) iodide by iodide ions, $I^-_{(aq)}$. $2Cu^{2+}_{(aq)} + 4I^-_{(aq)} \rightarrow 2CuI_{(s)} + I_{2(aq)}$

The resulting solution is brown, due to the dissolved I_2.

Disproportionation of Cu^+ ions

$Cu^+_{(aq)}$ is unstable and spontaneously disproportionates — this means it is oxidised and reduced at the same time. So if you have two Cu^+ ions, one gains an electron (is reduced) to become Cu, the other loses an electron (is oxidised) to become Cu^{2+}.

$$2Cu^+_{(aq)} \rightarrow Cu_{(s)} + Cu^{2+}_{(aq)}$$

Practice Questions — Fact Recall

Q1 Give an example of an oxidising agent which could be used in the conversion of Fe^{2+} to Fe^{3+}.

Q2 Aqueous hydrogen peroxide is added to an aqueous chromium(III) solution. Aqueous chromate(VI) ions are produced.

- a) What is the change in oxidation state when Cr^{3+} ions are oxidised to CrO_4^{2-} ions?
- b) What colour change is observed during this reaction?
- c) What would the product be if dilute sulfuric acid was added to the chromate(VI) solution?
- d) What colour change would be observed if dilute sulfuric acid was added to the chromate(VI) solution?

Q3 What does disproportionation mean?

Learning Objectives:

- Know how to carry out the qualitative analysis of ions on a test tube scale (PAG 4).
- Know the processes and techniques needed to identify the following anions in an unknown compound: CO_3^{2-}, Cl^-, Br^-, I^-, and SO_4^{2-}.
- Know the processes and techniques needed to identify the following cations in an unknown compound: NH_4^+, Cu^{2+}, Fe^{2+}, Fe^{3+}, Mn^{2+}, and Cr^{3+}.

Specification Reference 5.3.2

8. Tests for Ions

PRACTICAL ACTIVITY GROUP 4

It's really important that you know how to identify certain ions. You need to know the simple tests for some transition metal ions, as well as some common ions. You'll have come across some of these tests before so with any luck, this shouldn't be too tricky...

Identifying transition metal ions

Many transition metal ions form coloured precipitates when aqueous sodium hydroxide is added (see page 426). This is a good way to identify which transition metal ions are in a solution. To carry out the tests, add $NaOH_{(aq)}$ solution, dropwise from a pipette, to a test tube containing the unknown solution and record the colour of any precipitate formed. The table below shows some of the ions that can be identified using this method.

Ion	Observation
Cu^{2+}	pale blue precipitate
Fe^{2+}	pale green precipitate
Fe^{3+}	orange-brown precipitate
Mn^{2+}	pale brown precipitate
Cr^{3+}	dark green precipitate

Tip: Think about any safety precautions you might need to consider before doing these tests.

Test for halides

To test for halide ions just add nitric acid, then silver nitrate solution. If chloride, bromide or iodide is present, a precipitate will form. The colour of the precipitate depends on the halide present — silver chloride (AgCl) is a white precipitate, silver bromide (AgBr) is a cream precipitate and silver iodide (AgI) is a yellow precipitate.

Test for carbonates

To test an unknown solution for carbonates (CO_3^{2-}), add a dilute strong acid (e.g. dilute nitric acid or dilute hydrochloric acid). If carbonates are present then carbon dioxide will be released. To see if carbon dioxide is produced, you need to bubble any gas created through limewater. If carbon dioxide is present, then it'll turn the limewater cloudy (see Figure 1).

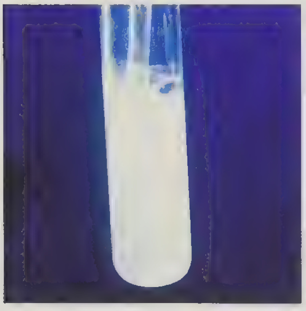


Figure 1: Limewater turns cloudy when carbon dioxide is added to it.

Example

Calcium carbonate reacts with hydrochloric acid to produce carbon dioxide, water and calcium chloride. The equation for this reaction is:

$$CaCO_{3(s)} + 2HCl_{(aq)} \rightarrow CO_{2(g)} + H_2O_{(l)} + CaCl_{2(aq)}$$

Test for sulfates

To test for sulfate ions (SO_4^{2-}), add a dilute strong acid followed by few drops of barium nitrate solution, $Ba(NO_3)_{2(aq)}$, to a solution of the unknown substance. If you get a white precipitate it will be barium sulfate, which tells you that there are sulfate ions in the solution (see Figure 2). You need to add the dilute acid to make sure you don't end up with a false positive due to carbonate or sulfite ions, which also produce a white precipitate when reacted with barium nitrate. Adding the acid removes any carbonates and sulfites present that might interfere with the test.

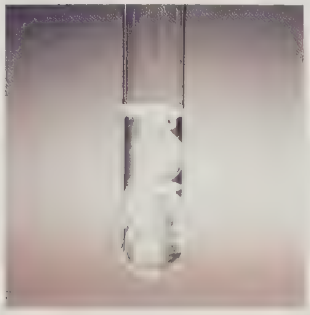


Figure 2: Barium sulfate is a white precipitate.

Example

Sodium sulfate reacts with $Ba(NO_3)_2$ solution to give barium sulfate and sodium nitrate:

$$Na_2SO_{4\,(aq)} + Ba(NO_3)_{2\,(aq)} \rightarrow BaSO_{4\,(s)} + 2NaNO_{3\,(aq)}$$

Tip: You could use barium chloride to test for sulfates instead of barium nitrate.

Test for ammonium ions

Ammonia gas (NH_3) is alkaline, so you can check for it using a damp piece of red litmus paper. If there's ammonia present, the paper will turn blue. You'll also be able to smell ammonia — it has a distinctive, pungent smell.

You can use this to test whether a substance contains ammonium ions (NH_4^+). Add a few drops of aqueous sodium hydroxide to your unknown substance in a test tube and warm the mixture. Hold a piece of damp litmus paper near the top of the test tube. If the paper turns blue it means ammonia is being given off and there are ammonium ions in your substance.

Tip: The litmus paper needs to be damp so the ammonia gas can dissolve and make the colour change.

Example

Ammonium chloride reacts with sodium hydroxide to give ammonia, water and sodium chloride.

$$NH_4Cl_{(aq)} + NaOH_{(aq)} \rightarrow NH_{3(g)} + H_2O + NaCl_{(aq)}$$

Practice Questions — Application

Q1 An unknown solution is put through a series of tests to determine which ions are present.
Firstly, $NaOH_{(aq)}$ is added. A pale blue precipitate is formed.
Secondly, dilute hydrochloric acid is added. The gas produced is delivered into limewater. The limewater goes cloudy.

Which ions are present in the unknown solution?

Q2 Two students add barium nitrate solution to an unknown solution to try and determine which ions are present. A white precipitate is formed. One student claims that this means sulfate ions are present in the solution. The other student claims that this means carbonate ions are present in the solution.

Comment on the conclusion of each student.

Exam Tip
If you're asked how to test for a particular ion in the exam, or you're asked to draw conclusions from a set of results, you need to think about what ions could be present that could give false positives. Have they been dealt with or could they interfere with the test? Also, remember to always consider the effect that adding substances during a test could have. Have ions been added that will affect the results?

Practice Questions — Fact Recall

Q1 Give the colour of the precipitate formed when $NaOH_{(aq)}$ is added to solutions of the following ions:

a) Mn^{2+}, b) Fe^{2+}, c) Cr^{3+}?

Q2 Name a dilute acid used in the test for:

a) carbonate ions b) halide ions

Q3 What colour will damp red litmus paper go in the presence of ammonium ions?

Section Summary

Make sure you know...

- That transition elements are d-block elements that have an ion with a partially filled d-sub-shell.
- That the elements Ti–Cu are transition elements.
- How to work out the electron configuration of atoms and ions of the d-block elements of Period 4 (Sc–Zn).
- Why scandium and zinc aren't transition elements.
- That transition elements can form complex ions.
- That transition elements can form coloured ions.
- That transition elements have variable oxidation states.
- That transition elements make great catalysts because of their variable oxidation states.
- The common colours of different transition metal ions and their oxidation states.
- That a complex ion is a metal ion surrounded by coordinately bonded ligands.
- That a ligand is an atom, ion or molecule that can form coordinate bonds with a central metal ion.
- That coordination number is the number of coordinate bonds formed with the central metal ion in a complex ion.
- What bidentate ligands are and that $NH_2CH_2CH_2NH_2$ (en) is a bidentate ligand.
- Examples of complexes with a coordination number of six and an octahedral shape.
- Examples of complexes with a coordination number of four and a tetrahedral or square planar shape.
- That complexes such as $[Ni(en)_3]^{2+}$ can show optical isomerism.
- That complexes such as $Pt(NH_3)_2Cl_2$ can show *cis-trans* isomerism.
- That cisplatin is used as an anti-cancer drug and how it works.
- That ligands can be substituted for one another in ligand substitution reactions.
- The ligand substitution reaction and the colour change for the formation of $[Cr(NH_3)_6]^{3+}$ from $[Cr(H_2O)_6]^{3+}$.
- The ligand substitution reactions and the colour changes for the formation of $[Cu(NH_3)_4(H_2O)_2]^{2+}$ and $[CuCl_4]^{2-}$ from $[Cu(H_2O)_6]^{2+}$.
- How the iron in haemoglobin allows oxygen to be transported around the body.
- Why the ligand substitution of oxygen or water for carbon monoxide in haemoglobin is so dangerous.
- The ionic equations for the precipitation reactions of $Cu^{2+}_{(aq)}$, $Mn^{2+}_{(aq)}$, $Fe^{2+}_{(aq)}$, $Fe^{3+}_{(aq)}$ and $Cr^{3+}_{(aq)}$ with aqueous sodium hydroxide or aqueous ammonia.
- The colour changes that happen when $Cu^{2+}_{(aq)}$, $Mn^{2+}_{(aq)}$, $Fe^{2+}_{(aq)}$, $Fe^{3+}_{(aq)}$ and $Cr^{3+}_{(aq)}$ react with aqueous sodium hydroxide or aqueous ammonia.
- The ionic equation and colour change when $Cu^{2+}_{(aq)}$ reacts with excess ammonia.
- The ionic equation and colour change when $Cr^{3+}_{(aq)}$ reacts with excess sodium hydroxide or excess ammonia.
- That transition elements can undergo redox reactions.
- The redox reactions in the interconversion between Fe^{2+} and Fe^{3+}.
- The redox reactions in the interconversion between Cr^{3+} and $Cr_2O_7^{2-}$.
- The redox reactions in the reduction of Cu^{2+} and the disproportionation of Cu^+.
- How to carry out tests to identify the following anions in unknown compounds: CO_3^{2-}, Cl^-, Br^-, I^-, and SO_4^{2-}.
- How to carry out tests to identify the following cations in unknown compounds: NH_4^+, Cu^{2+}, Fe^{2+}, Fe^{3+}, Mn^{2+}, and Cr^{3+}.

Exam-style Questions

1 Which of the following shows an incorrect electron configuration for the given transition element?

A vanadium: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^3\ 4s^2$

B chromium: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$

C manganese: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6\ 4s^1$

D iron: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6\ 4s^2$

(1 mark)

2 Which of the following statements about the transition metal complex $[Cu(H_2O)_6]^{2+}{}_{(aq)}$ is untrue?

A When chloride ions are added, a yellow square planar complex is formed.

B When $NaOH_{(aq)}$ is added, a pale blue precipitate is formed.

C When excess $NH_{3(aq)}$ is added, a dark blue solution is formed.

D $[Cu(H_2O)_6]^{2+}{}_{(aq)}$ is octahedral and pale blue in solution.

(1 mark)

3 A student is given an unknown solution containing a transition metal complex and asked to identify the ions present. The student carries out three tests on three separate samples, the results of which are shown below.

Test 1: A few drops of $NaOH_{(aq)}$ are added to the unknown solution and a dark green precipitate forms.

Test 2: Dilute nitric acid is added to the unknown solution. The gas produced was bubbled through limewater. No change was observed in the limewater.

Test 3: Nitric acid is added to the unknown solution, followed by silver nitrate. A white precipitate forms.

What is the formula of the unknown transition metal complex?

A $[FeCl_4]^{2-}$

B $Cr_2(CO_3)_3$

C $Fe_2(SO_4)_3$

D $[CrCl_4]^-$

(1 mark)

4 Brass is an alloy of mainly copper and zinc.

(a) Dissolving brass in acid produces a solution which contains aqueous copper ions.

(i) What colour is the aqueous Cu^{2+} ion?

(1 mark)

(ii) Write down the full electron configurations of the copper atom and the Cu^{2+} ion.

(2 marks)

(iii) Explain why the Cu^{2+} ion has the chemical properties associated with transition metal elements.

(1 mark)

(b) In the solution the $[Cu(H_2O)_6]^{2+}$ complex ion forms.

(i) In this complex ion, water acts as a ligand.
Explain the meaning of the term ligand.

(1 mark)

(ii) Draw the 3D structure of $[Cu(H_2O)_6]^{2+}$ and state its shape.

(2 marks)

(iii) What is the coordination number of this ion?

(1 mark)

5 Many complex ions exist as stereoisomers.

(a) $CoCl_2(NH_3)_2$ exists as two stereoisomers.

(i) Give the shape of the $CoCl_2(NH_3)_2$ ion.

(1 mark)

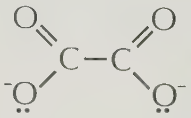
(ii) What type of stereoisomerism does $CoCl_2(NH_3)_2$ exhibit?

(1 mark)

(iii) Draw the two possible stereoisomers of $CoCl_2(NH_3)_2$.

(2 marks)

(b) The ethanedioate ion is a bidentate ligand. When it binds to chromium(III) ions it forms a complex ion with stereoisomers. The structure of the ethanedioate ion is shown below.



Ethanedioate ion

(i) What type of stereoisomerism does $[Cr(C_2O_4)_3]^{3-}$ exhibit?

(1 mark)

(ii) Describe how the ethanedioate ion bonds to the chromium ion.

(2 marks)

(iii) Draw two stereoisomers of $[Cr(C_2O_4)_3]^{3-}$.

(2 marks)

6 Fe^{2+} is a transition element ion that can undergo a wide variety of reactions.

(a) What is a transition element?

(1 mark)

(b) $Fe^{2+}_{(aq)}$ can react with sodium hydroxide to form a precipitate.

(i) Write down the ionic equation for this reaction.

(1 mark)

(ii) What colour is the precipitate?

(1 mark)

(c) Fe^{2+} can combine with ligands to form complex ions.

(i) Write an equation for the reaction between the hexaaqua iron(II) ion ($[Fe(H_2O)_6]^{2+}$) and $Cl^-_{(aq)}$ ions to form a tetrahedral complex.

(2 marks)

(ii) Draw the structure of the complex ion formed in part **(c) (i)**.

(1 mark)

(iii) The hexaaqua iron(II) ion will also react with six CN^- ions in a ligand substitution reaction. Write down the equation for this reaction.

(1 mark)

(iv) State whether you expect the coordination number, shape and/or colour of the complex ion to change during the reaction in **(c) (iii)**. Explain your answer.

(3 marks)

7 Hydrogen peroxide, $H_2O_{2(aq)}$, is used as an oxidising agent in the oxidation of $Cr(OH)_6{}^{3-}{}_{(aq)}$ to form $CrO_4{}^{2-}{}_{(aq)}$.

(a) $Cr(OH)_6{}^{3-}{}_{(aq)}$ is formed from $Cr^{3+}_{(aq)}$ ions.

(i) How can $Cr(OH)_6{}^{3-}{}_{(aq)}$ be formed from the hexaaqua chromium(III) ion?

(1 mark)

(ii) Write the balanced, full equation for the reaction in part **(a) (i)**.

(1 mark)

(b) The half-equations for the redox reaction between H_2O_2 and $Cr(OH)_6{}^{3-}$ are:

$$H_2O_2 + 2e^- \rightarrow 2OH^-$$

$$2Cr(OH)_6{}^{3-} + 4OH^- \rightarrow 2CrO_4{}^{2-} + 8H_2O + 6e^-$$

(i) Write the balanced, full equation for this redox reaction.

(1 mark)

(ii) How many moles of H_2O_2 are needed to fully oxidise 4 moles of $Cr(OH)_6{}^{3-}$?

(1 mark)

(iii) Describe the colour change that is observed during this reaction.

(1 mark)

(iv) Once chromate, $CrO_4{}^{2-}$, is formed, suggest a method to convert it to dichromate, $Cr_2O_7{}^{2-}$.

(1 mark)

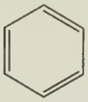
Module 6 Section 1: Aromatic Compounds and Carbonyls

Learning Objectives:

- Be able to compare the Kekulé and delocalised models of benzene in terms of p-orbital overlap forming a delocalised π-system.
- Understand the experimental evidence for a delocalised, rather than Kekulé, model for benzene in terms of bond lengths, enthalpy change of hydrogenation and resistance to reaction.
- Be able to use IUPAC rules of nomenclature for systematically naming substituted aromatic compounds.

Specification Reference 6.1.1

Tip: In skeletal structures like this one...



...there is a carbon atom at each corner and you work out the positions of the hydrogens by looking at the number of bonds coming from each carbon. There should be four — if there aren't, add one or more hydrogens.

Tip: pm stands for picometre. A picometre is 1×10^{-12} metres — that's very small indeed.

1. Benzene

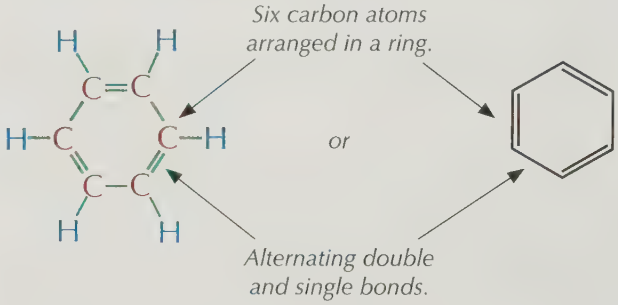
Benzene is one of the most important molecules in organic chemistry. Loads of exciting organic molecules contain benzene rings, like aspirin, morphine, dopamine and styrene (to name just a few).

What is benzene?

Benzene has the formula C_6H_6. It has a cyclic structure, as its six carbon atoms are joined together in a ring. The ring itself is planar (flat) and the hydrogens all stick out in the same plane. There are two main models to explain the structure of the benzene ring — the Kekulé model and the delocalised model.

The Kekulé model

This was proposed by German chemist Friedrich August Kekulé in 1865. He came up with the idea of a ring of C atoms with alternating single and double bonds between them (see Figure 1).



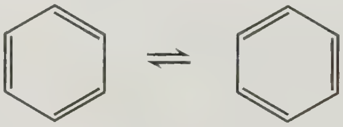
Six carbon atoms arranged in a ring.

or

Alternating double and single bonds.

Figure 1: *The structure of benzene according to Kekulé.*

He later adapted the model to say that the benzene molecule was constantly flipping between two forms (isomers) by switching over the double and single bonds (see Figure 2).



First benzene isomer

Second benzene isomer

Figure 2: *Benzene flipping between two forms in the adapted Kekulé model.*

HOW SCIENCE WORKS

If the Kekulé model was correct, you'd expect there to always be three bonds with the length of a C–C bond (154 pm) and three bonds with the length of a C=C bond (134 pm). However X-ray diffraction studies have shown that all the carbon-carbon bonds in benzene have the same length (140 pm) — they're between the length of a single bond and a double bond. So the Kekulé structure can't be quite right, but it's still used today as it's useful for drawing reaction mechanisms.

The delocalised model

The bond-length observations are explained by the **delocalised** model. In this model, the p-orbitals of all six carbon atoms overlap to create a π-system. This π-system is made up of two ring-shaped clouds of electrons — one above and one below the plane of the six carbon atoms (see Figure 3).

Tip: Check out page 107 if you're struggling to remember p-orbitals.

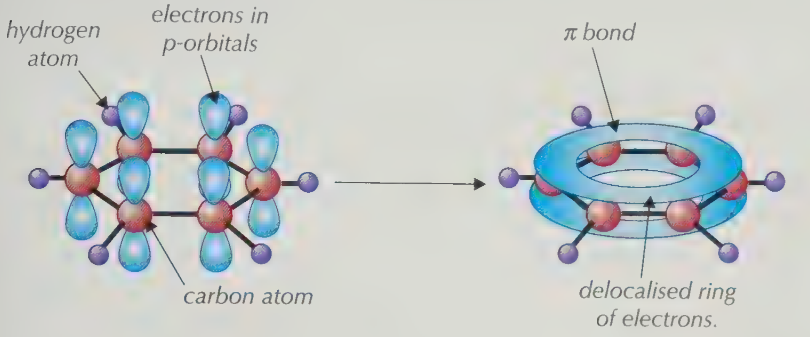

hydrogen atom
electrons in p-orbitals
π bond
carbon atom
delocalised ring of electrons.

Figure 3: *The formation of π bonds in benzene.*

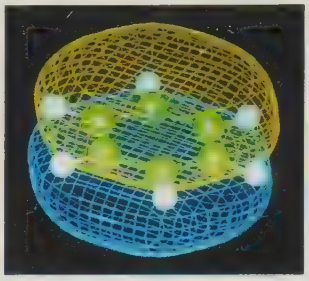


Figure 4: *A computer graphic showing the structure of benzene.*

All the carbon-carbon bonds in the ring are the same length because all the bonds are the same. The electrons in the rings are said to be delocalised because they don't belong to a specific carbon atom. They are represented as a circle in the ring of carbons rather than as double or single bonds (see Figure 5).

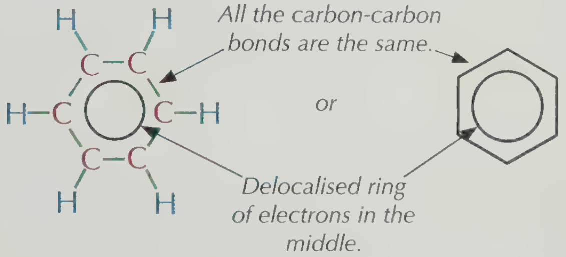

H
H
H–C
C–H
C–C
C–C
H
H
All the carbon-carbon bonds are the same.
or
Delocalised ring of electrons in the middle.

Figure 5: *The structure of benzene according to the delocalised model.*

Tip: There's lots more on models and theories in the How Science Works section (see pages 1-4).

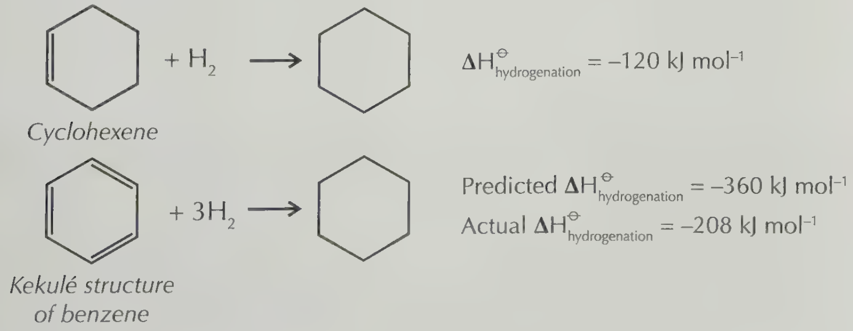
Evidence for delocalisation

If you react an alkene with hydrogen gas, two atoms of hydrogen add across the double bond. This is called **hydrogenation**, and the enthalpy change of the reaction is the enthalpy change of hydrogenation.

Cyclohexene has one double bond. When it's hydrogenated, the enthalpy change is –120 kJ mol^{-1}. If benzene had three double bonds (as in the Kekulé structure), you'd expect it to have an enthalpy of hydrogenation of –360 kJ mol^{-1}. But the experimental enthalpy of hydrogenation of benzene is –208 kJ mol^{-1} — far less exothermic than expected (see Figure 6).

Tip: If something's been hydrogenated it means that hydrogen has been added to it.

Tip: See page 363 for more on enthalpy.


$+ H_2$
Cyclohexene
$+ 3H_2$
Kekulé structure of benzene

$\Delta H^{\ominus}_{\text{hydrogenation}} = -120 \text{ kJ mol}^{-1}$

Predicted $\Delta H^{\ominus}_{\text{hydrogenation}} = -360 \text{ kJ mol}^{-1}$

Actual $\Delta H^{\ominus}_{\text{hydrogenation}} = -208 \text{ kJ mol}^{-1}$

Figure 6: *Enthalpies of hydrogenation for cyclohexene and benzene.*

Exam Tip
For the exam you need to know three pieces of evidence for the delocalised model of benzene — bond length data (page 436), enthalpy change data (page 437) and the fact that benzene is relatively unreactive (there's more about this coming up on page 440).

Energy is put in to break bonds and released when bonds are made. So more energy must have been put in to break the bonds in benzene than would be needed to break the bonds in the Kekulé structure. This difference indicates that benzene is more stable than the Kekulé structure would be. This is thought to be due to the delocalised ring of electrons. In a delocalised ring the electron density is shared over more atoms, which means that the molecule is more stable.

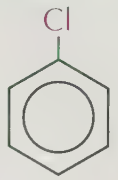
Naming aromatic compounds

Compounds containing a benzene ring are called arenes or '**aromatic compounds**'. Aromatic compounds all contain a benzene ring. Naming them can be a bit tricky. They're named in two ways:

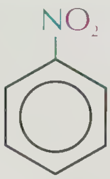
1. In some cases, the benzene ring is the main functional group and the molecule is named as a substituted benzene ring — the suffix is -benzene and there are prefixes to represent any other functional groups.

Tip: Non-aromatic molecules are called aliphatic molecules — don't get the terms aromatic and aliphatic mixed up.

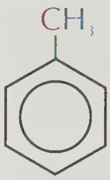
Examples



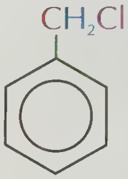
Chlorobenzene



Nitrobenzene



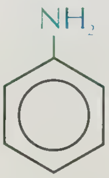
Methylbenzene



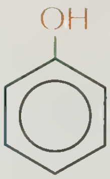
Chloromethylbenzene

2. In other cases, the benzene ring is not the main functional group and the molecule is named as having a phenyl group (C_6H_5) attached. Phenyl- is used as a prefix to show the molecule has a benzene ring and the suffix comes from other functional groups on the molecule (e.g. -ol if it's an alcohol, -amine if it's an amine).

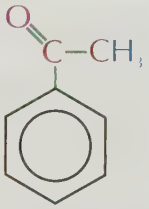
Examples



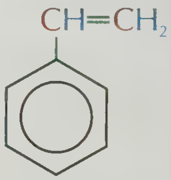
Phenylamine



Phenol



Phenylethanone



Phenylethene

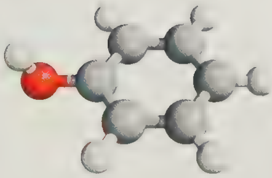


Figure 7: *A molecular model of phenol.*

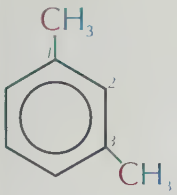
Unfortunately there's no simple rule to help you remember which molecules should be something –benzene and which molecules should be phenyl–something. You just have to learn these examples.

Numbering the benzene ring

If there is more than one functional group attached to the benzene ring, you have to number the carbons to show where the groups are. If all the functional groups are the same, pick any group to start from and count round either clockwise or anticlockwise — whichever way gives the smallest numbers. If the functional groups are different, start from whichever functional group gives the molecule its suffix (e.g. the –OH group for a phenol) and continue counting round whichever way gives the smallest numbers.

Tip: If there is only one functional group you don't have to number the carbons because all the positions around the carbon ring are the same.

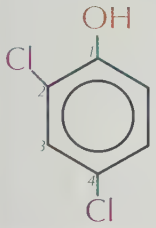
Examples



This benzene ring only has methyl groups attached so it will be named as a substituted benzene ring.

Starting from the methyl group at the top and counting clockwise there is another methyl group on carbon-3.

So this is 1,3-dimethylbenzene.



This benzene ring has an OH group attached so the stem is phenol.

Starting from the OH group (the group which gives the molecule its name) and counting anticlockwise there are chlorines on carbon-2 and carbon-4.

So this is 2,4-dichlorophenol.

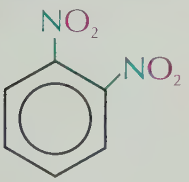
Exam Tip

You're unlikely to be asked to name anything too complicated in the exam. If you need to give the product of a reaction, don't try and name it unless they specifically ask for the name — giving the structure should be enough to get the marks.

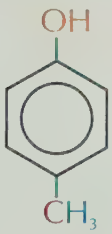
Practice Questions — Application

Q1 Name these aromatic compounds:

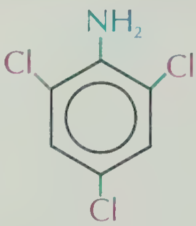
a)



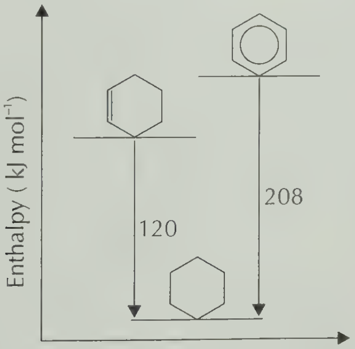
b)



c)



Q2 The graph below shows the enthalpies of hydrogenation of cyclohexene and benzene.



a) Describe Kekulé's model for the structure of benzene.

b) Use the information in the graph to explain why Kekulé's model for the structure of benzene was incorrect.

Practice Questions — Fact Recall

Q1 Describe the structure of benzene according to the delocalised model.

Q2 Explain how information on the bond lengths in benzene provides support for the delocalisation model.

Q3 What are aromatic compounds?

2. Reactions of Benzene

There are quite a few reactions that chemists can use to add different functional groups to benzene — that's what makes it so good as a starting point for making other compounds. Some reactions that you need to know are coming up...

Learning Objectives:

- Be able to explain the relative resistance to bromination of benzene, compared with alkenes, in terms of the delocalised electron density of the π-system in benzene compared with the localised electron density of the π-bond in alkenes.
- Be able to describe the mechanism of electrophilic substitution of aromatic compounds with a halogen in the presence of a halogen carrier.
- Be able to describe the mechanism of electrophilic substitution of aromatic compounds with concentrated nitric acid in the presence of concentrated sulfuric acid.
- Be able to interpret unfamiliar electrophilic substitution reactions of aromatic compounds, including prediction of mechanisms.

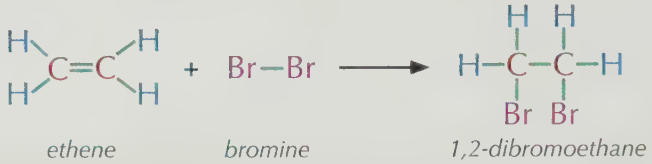
Specification Reference 6.1.1

Alkenes, benzene and addition reactions

Alkenes react easily with bromine water at room temperature. The reaction is the basis of the test for a double bond, as the orange colour of the bromine water is lost. It's an addition reaction — bromine atoms are added to the alkene.

Example

Ethene will react with bromine water in an electrophilic addition reaction.



This reaction occurs because the alkene C=C bond is a localised area of high electron density — it attracts an electrophile which adds to the double bond.

If the Kekulé structure (see page 436) was correct, you'd expect a similar reaction between benzene and bromine. In fact, to make it happen you need hot benzene and ultraviolet light — and it's still a real struggle.

This difference between benzene and other alkenes is explained by the π-system in benzene — the delocalised electron rings above and below the plane of carbon atoms (see page 437). They make the benzene ring very stable, and spread out the negative charge. So benzene is very unwilling to undergo addition reactions which would destroy the stable ring.

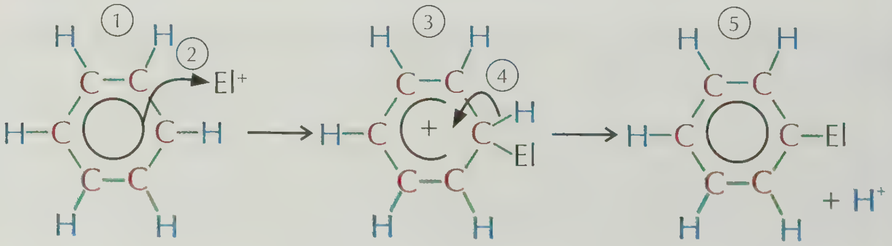
So, in alkenes, addition reactions occur across C=C bonds as electrophiles react with them to form stable alkanes. In benzene, this reaction isn't as favourable because the benzene ring is so stable and the negative charge is spread out. So benzene prefers to react by **electrophilic substitution**.

Tip: Benzene's stability and reluctance to undergo addition reactions is further evidence for the delocalised model (see page 437).

Electrophilic substitution

The benzene ring is a region of high electron density, so it attracts **electrophiles**. Electrophiles are electron pair acceptors — they are usually electron deficient (short of electrons) so are attracted to areas of high electron density. Common electrophiles include positively charged ions (e.g. H^+ or NO_2^+), and polar molecules (e.g. carbonyl compounds), which have a partial positive charge.

As the benzene ring's so stable, it tends to undergo electrophilic substitution reactions, which preserve the delocalised ring. The general mechanism for electrophilic substitution on a benzene ring is shown below:



Tip: Remember, electrophiles are positively charged ions or polar molecules that are attracted to areas of negative charge.

1. The electron dense region at the centre of the benzene ring attracts an electrophile (El^+).
2. The electrophile steals a pair of electrons from the centre of the benzene ring and forms a bond with one of the carbons.
3. This partially breaks the delocalised electron ring and gives the molecule a positive charge.
4. To regain the stability of the benzene ring, the carbon which is now bound to the electrophile loses a hydrogen.
5. So you get the substitution of an H^+ with the electrophile.

You need to know two electrophilic substitution mechanisms for benzene — halogenation using a halogen carrier (below) and the nitration reaction (see page 442).

Tip: Don't get confused between electrophiles and nucleophiles. Just remember, electrophiles love electrons.

Tip: The horseshoe shape in the centre of the benzene ring in step three of the mechanism is just showing that the delocalisation of electrons around the ring has been partially broken.

Halogenation using a halogen carrier

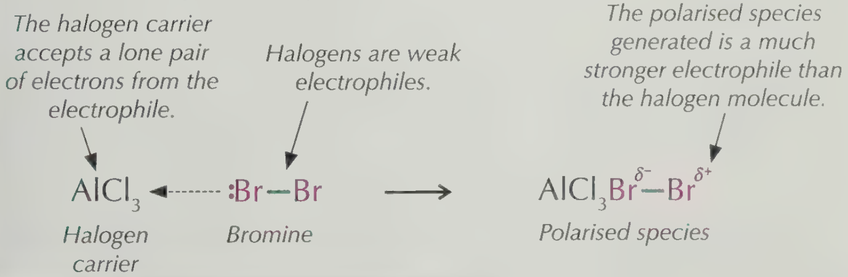
A **halogen carrier** can be used to add a halogen atom onto a benzene ring via an electrophilic substitution reaction. Without the halogen carrier, the electrophile doesn't have a strong enough positive charge to attack the stable benzene ring. Here's a bit about how halogen carriers work:

Halogen carriers make the electrophile stronger by accepting a lone pair of electrons from the electrophile. As the lone pair of electrons is pulled away, the polarisation in the electrophile increases and a permanent dipole forms. This makes it a much, much stronger electrophile, and gives it a strong enough charge to react with the benzene ring. Examples of halogen carriers include aluminium halides (e.g. $AlCl_3$), iron halides (e.g. $FeCl_3$) and iron.

Tip: It'll help if you remember the mechanism has two steps — addition of the electrophile to form a positively charged intermediate, followed by loss of H^+ from the carbon atom attached to the electrophile.

Example

Aluminium chloride can combine with a bromine molecule to form a more reactive polarised species.



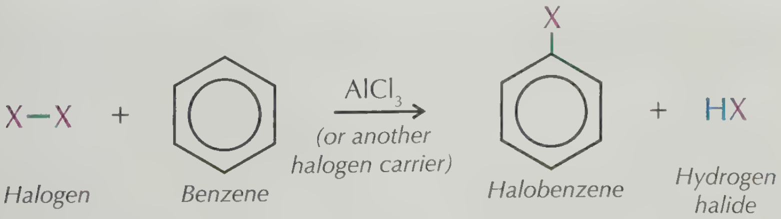
The halogen carrier accepts a lone pair of electrons from the electrophile.

Halogens are weak electrophiles.

The polarised species generated is a much stronger electrophile than the halogen molecule.

Tip: Chlorine will react with aluminium chloride in exactly the same way.

Here's the overall equation for a halogenation reaction using a halogen carrier:



Tip: The halogen carrier acts as a catalyst — it speeds up the reaction without being used up.

And here's an example of an electrophilic substitution reaction using a halogen carrier:

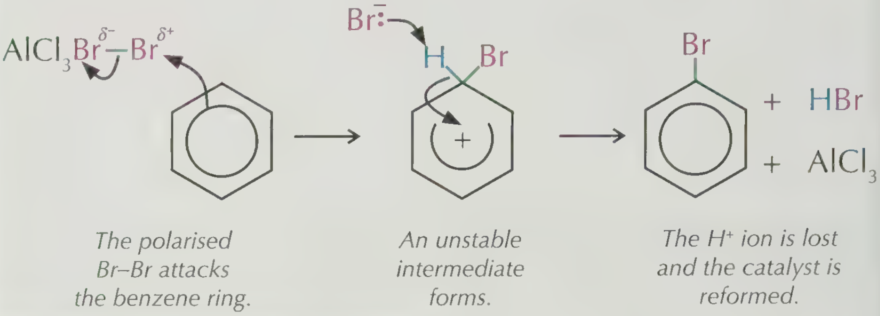
Example

Benzene will react with bromine, Br–Br, in the presence of aluminium chloride, $AlCl_3$. Br–Br is the electrophile. $AlCl_3$ acts as the halogen carrier. A Br atom is substituted in place of a H atom.

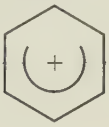
Tip: The H in the hydrogen halide is the one that's been kicked off the benzene ring (and replaced with an X).

Electrons in the benzene ring are attracted to the partially positively charged bromine atom. Two electrons from the benzene bond with the bromine, the Br–Br bond is broken and a Br^- ion is formed. This partially breaks the delocalised ring and gives it a positive charge.

The negatively charged Br^- ion bonds with the hydrogen. This removes the hydrogen from the ring, forming HBr and bromobenzene.


$AlCl_3Br^{\delta-}–Br^{\delta+}$
Br^-
H
Br
+
Br
+ HBr
+ $AlCl_3$
The polarised Br–Br attacks the benzene ring.
An unstable intermediate forms.
The H^+ ion is lost and the catalyst is reformed.

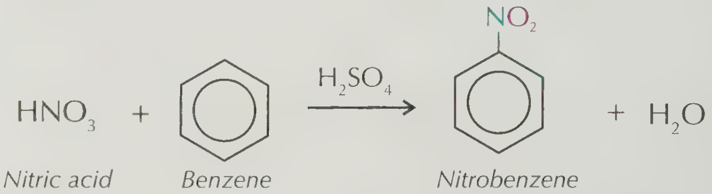
Exam Tip
When drawing the intermediates of these reactions, make sure the horseshoe in the middle of the benzene ring comes over half way up:



If you make it any smaller you'll lose marks.

Nitration

When you warm benzene with concentrated nitric acid and concentrated sulfuric acid, you get nitrobenzene. The overall equation for this reaction is:


HNO_3
+
H_2SO_4
NO_2
+ H_2O
Nitric acid
Benzene
Nitrobenzene

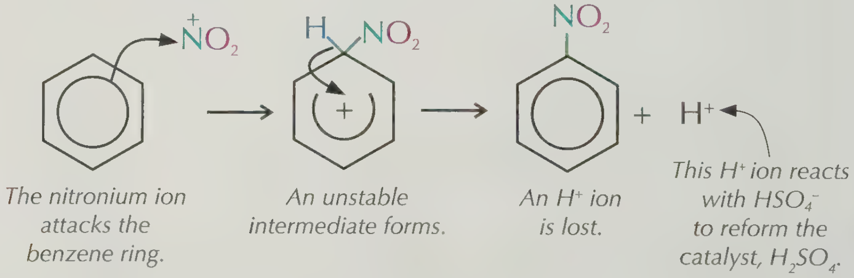
Tip: This mechanism works for other arenes too, not just benzene. Take a look at the next page for an example.

Sulfuric acid acts as a catalyst — it helps to make the nitronium ion, NO_2^+, which is the electrophile. The formation of the nitronium ion is the first step of the reaction mechanism. The equation for this reaction is shown below:

$$\mathbf{HNO_3 + H_2SO_4 \rightarrow HSO_4^- + NO_2^+ + H_2O}$$

Exam Tip
In the exam, you might be asked to write out the equation for the formation of the nitronium ion before giving the rest of the mechanism for nitration — so make sure you learn it.

Once the nitronium ion has been formed, it can react with benzene to form nitrobenzene. This is the electrophilic substitution step in the reaction. Here's the mechanism for the electrophilic substitution part of the reaction:


$\overset{+}{N}O_2$
H
NO_2
+
NO_2
+ H^+
The nitronium ion attacks the benzene ring.
An unstable intermediate forms.
An H^+ ion is lost.
This H^+ ion reacts with HSO_4^- to reform the catalyst, H_2SO_4.

If you only want one NO_2 group added (mononitration), you need to keep the temperature below 55 °C. Above this temperature you'll get lots of substitutions.

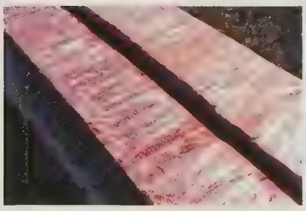
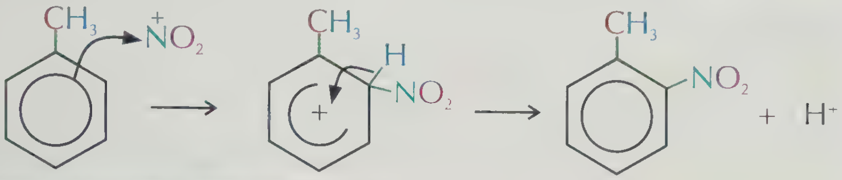


Figure 1: Blocks of TNT explosives. Substitution of three hydrogen atoms for NO_2 groups on a methylbenzene molecule will produce TNT.

Example

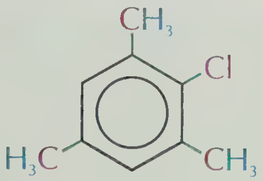
Warming methylbenzene with concentrated nitric acid and concentrated sulfuric acid at a temperature below 55 °C will produce 1-methyl-2-nitrobenzene.



Tip: This reaction will produce some 1-methyl-2-nitrobenzene, some 1-methyl-3-nitrobenzene and some 1-methyl-4-nitrobenzene. But the majority of the product formed will be the 1-methyl-2-nitrobenzene. The reasons for this are quite complicated and you don't need to know them for A Level (but if you're interested ask your teacher...).

Practice Questions — Application

Q1 The structure of 1-chloro-2,4,6-trimethylbenzene is shown below.



a) Write out the equation for the production of 1-chloro-2,4,6-trimethylbenzene from 1,3,5-trimethylbenzene and chlorine.

b) Suggest a suitable catalyst for this reaction.

c) Outline the mechanism for this reaction.

Q2 a) Draw the mechanism for the formation of nitrobenzene from benzene and concentrated nitric acid.

b) What two conditions are needed for this reaction to occur?

Q3 A scientist is trying to create the explosive TNT. The IUPAC name for TNT is 1-methyl-2,4,6-trinitrobenzene.

a) Draw the structure of TNT.

b) The scientist uses a nitration reaction to create TNT. What is important about the temperature that the reaction is carried out at? Explain your answer.

Exam Tip
Examiners can be tricksy and you might have to draw a mechanism for an odd looking molecule in the exam. Don't panic. All electrophilic substitution reaction mechanisms are the same — use the steps shown on the previous pages and make sure your equation is balanced and you'll be fine.

Practice Questions — Fact Recall

Q1 Explain why alkenes will react via addition reactions at room temperature but benzene won't.

Q2 Explain why electrophiles are attracted to aromatic compounds.

Q3 a) Give two examples of halogen carriers.

b) Explain why halogen carriers are needed for benzene to react with Br_2.

Q4 Write an equation to show the formation of a nitronium ion (NO_2^+) from chemical reagents.

Tip: A reagent is a chemical that can be used straight out of a bottle or container.

3. Friedel-Crafts

Because benzene is so stable, it's fairly unreactive. Friedel-Crafts is a useful process for overcoming this problem.

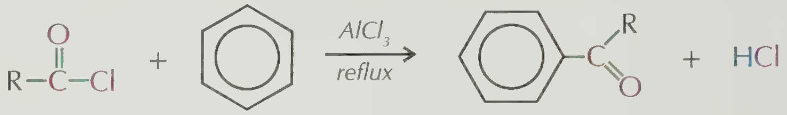
Learning Objective:

- Be able to describe the electrophilic substitution of aromatic compounds with a haloalkane or acyl chloride in the presence of a halogen carrier (Friedel-Crafts reaction) and its importance to synthesis by formation of a C–C bond to an aromatic ring.

Specification Reference 6.1.1

Acylation

Friedel-Crafts acylation is used to add an acyl group (–C(=O)–R) to the benzene ring. It results in the formation of a new C–C bond, which are difficult to make, and so this reaction is important in organic synthesis. Once an acyl group has been added, the side chains can be modified by further reactions to produce useful products, making this a very versatile reaction in organic synthesis. The products of the reaction are HCl and a phenylketone. The reactants need to be heated under reflux in a non-aqueous environment for the reaction to occur. Here's the equation for the reaction:



Acyl chloride *Benzene* *Phenylketone*

***Figure 1:** Charles Friedel — co-developer of Friedel-Crafts acylation.*

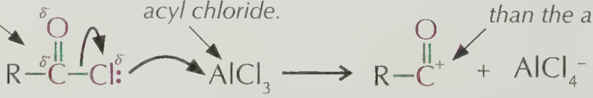
An electrophile has to have a pretty strong positive charge to be able to attack the stable benzene ring — most just aren't polarised enough. But some can be made into stronger electrophiles using a catalyst called a **halogen carrier**.

Friedel-Crafts acylation uses an acyl chloride to provide the electrophile and a halogen carrier such as $AlCl_3$. $AlCl_3$ accepts a lone pair of electrons from the acyl chloride. As the lone pair of electrons is pulled away, the polarisation in the acyl chloride increases and it forms a carbocation. This makes it a much, much stronger electrophile, and gives it a strong enough charge to react with the benzene ring. The formation of the carbocation is the first step in the reaction mechanism and is shown below:

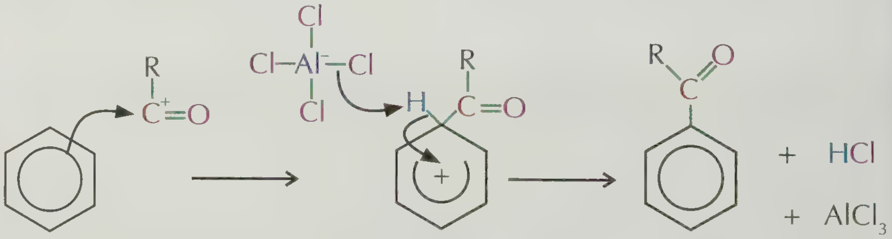
Acyl chlorides are weak electrophiles.

The halogen carrier accepts a lone pair of electrons from the acyl chloride.

The carbocation generated is a much stronger electrophile than the acyl chloride.



And here's the second step in the reaction mechanism, the electrophilic substitution bit:



Electrons in the benzene ring are attracted to the positively charged carbocation. Two electrons from the benzene bond with the carbocation. This partially breaks the delocalised ring and gives it a positive charge.

The negatively charged $AlCl_4^-$ ion is attracted to the positively charged ring. One chloride ion breaks away from the aluminium chloride ion and bonds with the hydrogen. This removes the hydrogen from the ring, forming HCl. It also allows the catalyst to reform. Any acyl chloride can react with benzene in this way.

Tip: A phenylketone is produced, unless R is just H, in which case an aldehyde called benzenecarbaldehyde, or benzaldehyde, is formed.

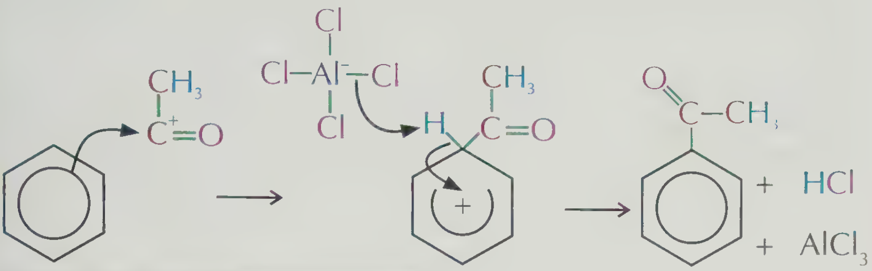
Exam Tip

You could draw out the full structure of benzene when writing out this equation — but these simplified diagrams are a lot quicker and could save you valuable time in your exam.

Example

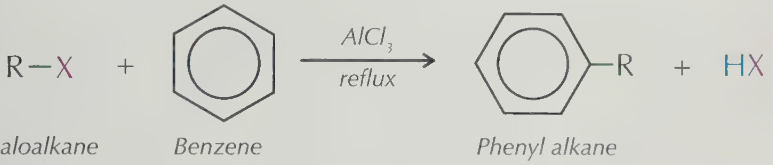
Ethanoyl chloride reacts with benzene to produce phenyl ethanone:

$$CH_3COCl + AlCl_3 \rightarrow CH_3CO^+ + AlCl_4^-$$



Alkylation

The Friedel-Crafts alkylation reaction works very much like the acylation reaction — except instead of putting an acyl group onto a benzene ring, it's an alkyl group. Here's the general equation for the reaction.

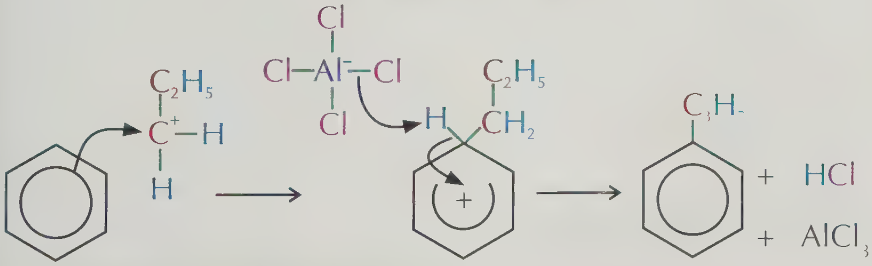


And to show you just how similar alkylation is to acylation, here's an example showing the mechanism.

Example

1-chloropropane reacts with benzene to produce propylbenzene:

$$C_3H_7Cl + AlCl_3 \rightarrow C_3H_7^+ + AlCl_4^-$$



Exam Tip

When drawing these mechanisms in your exam, make sure your curly arrows clearly go from the delocalised ring of electrons to the carbocation and from the C-H bond back to the delocalised electron ring. Just drawing your curly arrows to/from the centre of benzene won't be enough to get you all the marks.

Practice Question — Application

Q1 Phenylmethanal can be produced using Friedel-Crafts acylation.

a) Write out an equation for this reaction.

b) Suggest a suitable catalyst for this reaction.

c) Name and outline the mechanism for this reaction.

Practice Questions — Fact Recall

Q1 Why are Friedel-Crafts reactions important to synthesis?

Q2 Explain the role of $AlCl_3$ in Friedel-Crafts acylation.

4. Substituted Benzene Rings

Learning Objectives:

- Be able to use IUPAC rules of nomenclature for systematically naming phenols.
- Understand the weak acidity of phenols shown by the neutralisation reaction with NaOH but absence of reaction with carbonates.
- Understand the relative ease of electrophilic substitution of phenol compared with benzene, in terms of electron pair donation to the π-system from an oxygen p-orbital in phenol.
- Be able to describe the electrophilic substitution reactions of phenol with bromine to form 2,4,6-tribromophenol, and with dilute nitric acid to form 2-nitrophenol.
- Understand the 2- and 4-directing effect of electron-donating groups (OH, NH_2) and the 3-directing effect of electron-withdrawing groups (NO_2) in electrophilic substitution of aromatic compounds.
- Be able to predict the substitution products of aromatic compounds by directing effects and the importance to organic synthesis.

Specification Reference 6.1.1

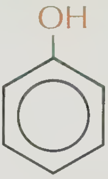
Substituted benzene rings are just benzene rings with one or more hydrogens replaced by something else. For example, phenols have an –OH group attached to a benzene ring. This gives them different properties to benzene.

Phenols

Phenol has the formula C_6H_5OH. Other phenols have various groups attached to the benzene ring.

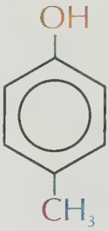
Examples

Here's the structure of phenol:



phenol

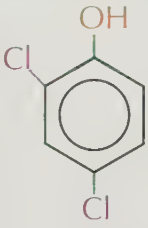
And here's the structure of 4-methylphenol:



4-methylphenol

Phenols are named in a very similar way to alcohols except you add the suffix -phenol instead of -ol. You have to number the carbon atoms too — the carbon with the –OH group attached is always carbon-1.

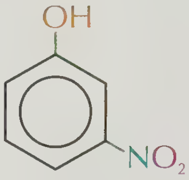
Examples



2,4-dichlorophenol

The phenol has two chlorine groups, one on carbon-2 and one on carbon-4. So this phenol is 2,4-dichlorophenol.

The phenol has a nitro group on carbon-3. So this phenol is 3-nitrophenol.



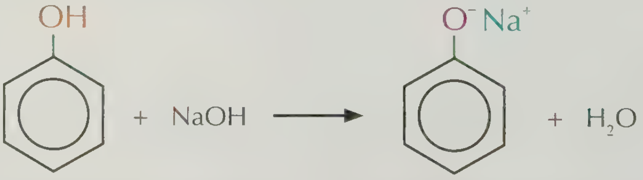
3-nitrophenol

Phenol reactions

Phenol is weakly acidic, so will undergo typical acid-base reactions.

acid + base → salt + water

Phenol reacts with sodium hydroxide solution at room temperature to form sodium phenoxide and water.



phenol *sodium phenoxide*

Phenol doesn't react with sodium carbonate solution though. Sodium carbonate is not a strong enough base and so can't remove the hydrogen ion from the oxygen atom.

Electrophilic substitution

If you shake phenol with orange bromine water, it will undergo an electrophilic substitution reaction — bromine atoms will be added to the phenol ring. Benzene doesn't react with bromine water (see page 440), so phenol's reaction must be to do with the OH group.

During the reaction, one of the lone pairs of electrons in a p-orbital of the oxygen atom overlaps with the delocalised ring of electrons in the benzene ring (see Figure 1) — this pair of electrons is partially delocalised into the π-system. This increases the electron density of the ring, making it more likely than benzene to be attacked by electrophiles.

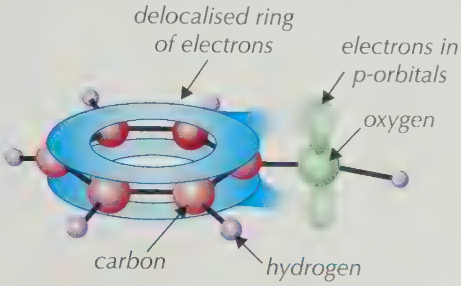


Figure 1: *The orbital overlap during the reaction of phenol with bromine.*

Electron-donating groups

In an unsubstituted benzene ring, all the carbon atoms are the same so electrophiles can react with any of them. If you have a substituted benzene ring, such as phenol, the functional group can change the electron density at certain carbon atoms, making them more or less likely to be react.

Electron-donating groups include –OH and $-NH_2$ — they have electrons in orbitals that overlap with the delocalised ring and increase its electron density. In particular, they increase the electron density at carbons 2-, 4- and 6-, so electrophiles are most likely to react at these positions (see Figure 2).

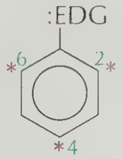
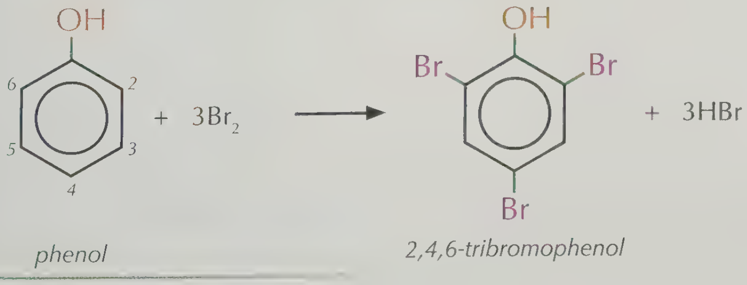


Figure 2: *The expected positions of electrophiles added onto a benzene with an electron-donating group.*

Example

The hydrogen atoms at 2, 4 and 6 are substituted by bromine atoms. The product is called 2,4,6-tribromophenol — it's insoluble in water and precipitates out of the mixture to form a white solid (see Figure 3). It smells of antiseptic.



Tip: EDG is an electron donating group, such as –OH or $-NH_2$.

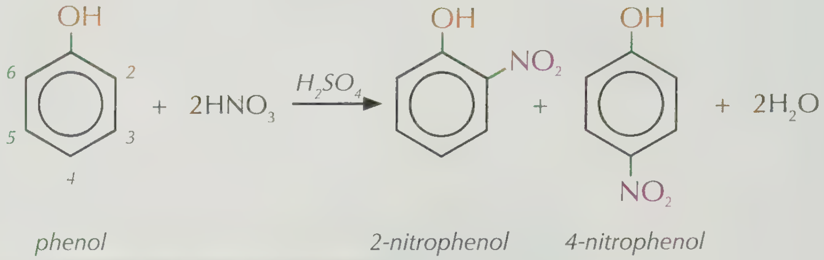
Figure 3: *Bromination of phenol. The reaction of phenol with bromine produces 2,4,6-tribromophenol, a white precipitate.*

Exam Tip

Don't forget to mention electron density when you're answering exam questions on the reactivity of phenol — it's the increased electron density in the ring that allows the bromine to react with phenol.

Example

Phenol reacts with dilute nitric acid to give two isomers of nitrophenol, and water. Nitrating phenol is much easier than nitrating benzene — that requires concentrated nitric acid and a concentrated sulfuric acid catalyst. The difference is due to the activating effect of the OH group again — and that's also why you're most likely to get NO_2 groups at positions 2 and 4 on the carbon ring.



Electron-withdrawing groups

$-NO_2$ is an electron-withdrawing group. It doesn't have any orbitals that can overlap with the delocalised ring and it's electronegative, so it withdraws electron density from the ring.

In particular, it withdraws electron density at carbons 2-,4- and 6-, so electrophiles are unlikely to react at these positions. This has the effect of directing electrophilic substitution to the 3- and 5- positions (see Figure 4).

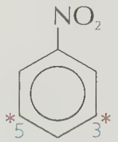
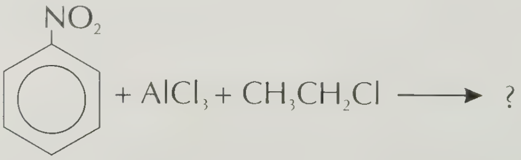


Figure 4: The expected positions of electrophiles added onto a benzene with an electron withdrawing group.

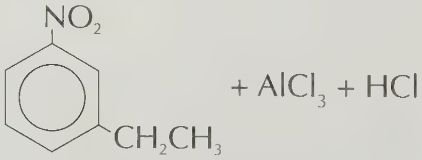
Knowing about electron-donating and electron-withdrawing groups means you can predict the properties of electrophilic substituted reactions.

Example

Predict the product of the following reaction:



$-NO_2$ is electron-withdrawing, so directs electrophilic substitution to carbon 3. The product is 3-ethylnitrobenzene:



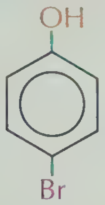
The benzene ring's only substituted once, so it doesn't matter whether you number the carbons clockwise or anticlockwise. This means the 3- and the 5- positions are the same.

Tip: The $AlCl_3$ here is just a halogen carrier — see p.441.

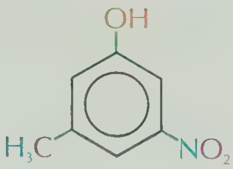
Practice Questions — Application

Q1 Name the following phenols:

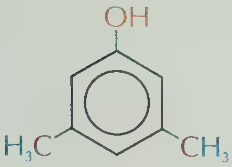
a)



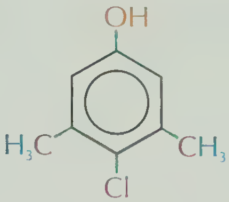
b)



c)



d)



Q2 Write equations for the reaction of each of the phenols in Q1 with $NaOH_{(aq)}$ at room temperature.

Q3 Describe what would happen if you reacted 2-methylphenol with sodium carbonate.

Q4 Trifluoromethylbenzene reacts with an excess of fluorine. The trifluoromethyl group is an electron withdrawing group. Draw the organic product of the reaction.

Tip: Remember that when you name molecules you write the prefixes in alphabetical order — for example, ethyl comes before methyl. (You ignore any di- or tri- bits though — for example, ethyl comes before dimethyl.)

Practice Questions — Fact Recall

Q1 Explain why phenol will react with bromine water but benzene won't.

Q2 Draw the structure of the organic product that forms when phenol reacts with bromine water.

Q3 a) Give an example of an electron-withdrawing group.

b) Give two examples of electron-donating groups.

Learning Objective:

- Be able to describe the oxidation of aldehydes using $Cr_2O_7^{2-}/H^+$ (i.e. $K_2Cr_2O_7/H_2SO_4$) to form carboxylic acids (PAG 7).

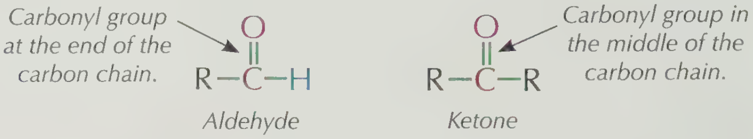
Specification Reference 6.1.2

5. Aldehydes and Ketones

Aldehydes and ketones are compounds that are made by oxidising alcohols. You've met aldehydes and ketones before, but just in case you can't remember, here's a quick review...

What are aldehydes and ketones?

Aldehydes and **ketones** are both **carbonyl compounds** as they both contain the carbonyl functional group, C=O. The difference is, they've got their carbonyl groups in different positions. Aldehydes have their carbonyl group at the end of the carbon chain. Ketones have their carbonyl group in the middle of the carbon chain, see Figure 1.


Carbonyl group at the end of the carbon chain.
Aldehyde
Ketone
Carbonyl group in the middle of the carbon chain.

$$R-\overset{\overset{\large O}{\|}}{C}-H \qquad R-\overset{\overset{\large O}{\|}}{C}-R$$

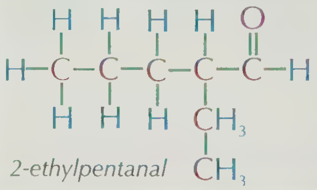
Figure 1: *The difference between an aldehyde and a ketone. 'R' represents a carbon chain of any length.*

Tip: This is all a recap of stuff you learnt in Module 4: Section 2, so if it doesn't seem familiar, have a look at pages 249-250.

Nomenclature

Aldehydes have the suffix -al. You don't have to say which carbon the functional group is on — it's always on carbon-1. Naming aldehydes follows very similar rules to the naming of alcohols.

Example



2-ethylpentanal

The longest carbon chain containing the aldehyde functional group is 5 carbon atoms, so the stem is pentane.

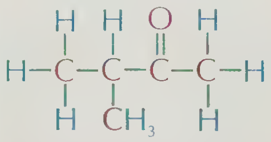
There's an ethyl- group attached to the second carbon atom so there's a 2-ethyl- prefix.

So, the aldehyde is called 2-ethylpentanal.

Tip: When naming ketones, the carbonyl group has the highest priority. So you always number the carbons from the end that means the carbonyl group carbon has the lowest number possible.

The suffix for ketones is -one. For ketones with five or more carbons, you always have to say which carbon the functional group is on. (If there are other groups attached, such as methyl groups, you have to say it for four-carbon ketones too.)

Example



3-methylbutan-2-one

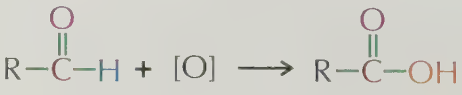
The longest continuous carbon chain is 4 carbon atoms, so the stem is butane.

The carbonyl is found on the second carbon atom and there is a methyl group on the third carbon.

So, the ketone is called 3-methylbutan-2-one.

Oxidising aldehydes

Aldehydes can be easily oxidised to carboxylic acids because there's a hydrogen attached to the carbonyl group:

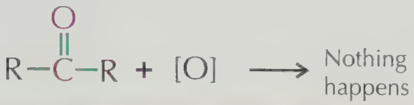


$$R-\overset{\overset{\large O}{\|}}{C}-H + [O] \longrightarrow R-\overset{\overset{\large O}{\|}}{C}-OH$$

You can oxidise aldehydes using the same conditions as for oxidising alcohols — you need to reflux them with an oxidising agent such as acidified potassium dichromate(VI) ($K_2Cr_2O_7/H_2SO_4$).

PRACTICAL ACTIVITY GROUP 7

The only way to oxidise a ketone would be to break a carbon-carbon bond so ketones are not easily oxidised:



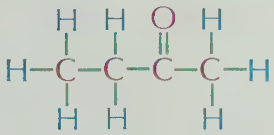
$$\text{R}-\overset{\overset{\text{O}}{\|}}{\text{C}}-\text{R} + [\text{O}] \longrightarrow \text{Nothing happens}$$

Tip: You learnt about oxidising alcohols in Module 4: Section 2 — check back if you need a reminder.

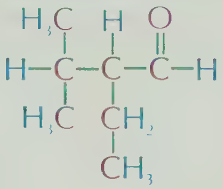
Practice Questions — Application

Q1 Name these molecules:

a)



b)

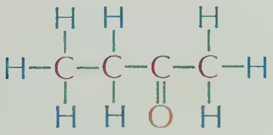


Tip: Remember, when you're naming molecules, the carbon attached to the group that gives the molecule its name (e.g. the –OH group in an alcohol) must be included in the chain used to find the stem of the name. Even if it's not the longest carbon chain in the molecule.

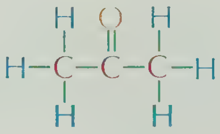
Q2 One of the molecules in Q1 can be oxidised with acidified potassium dichromate(VI). Which molecule can be oxidised, and what is the product of this oxidation?

Q3 Which of the carbonyls (**A**-**D**) below can be oxidised to carboxylic acids?

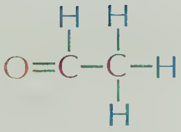
A



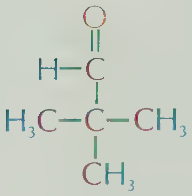
B



C



D



Q4 Write an equation for the oxidation of ethanal to ethanoic acid.

Tip: You can use [O] to stand for the oxidising agent in questions 4 (phew...).

Practice Questions — Fact Recall

Q1 What is the difference between an aldehyde and a ketone?

Q2 Give the molecular formula of the negative ion that is found in potassium dichromate(VI).

Q3 What type of compound is produced when an aldehyde is oxidised?

6. Reducing Carbonyls

Reduction is the opposite of oxidation. So you can reduce aldehydes, ketones and carboxylic acids to alcohols. Read on for a bit more detail...

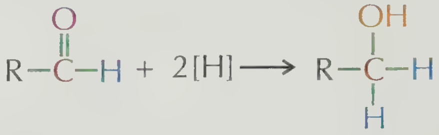
Learning Objectives:

- Be able to describe nucleophilic addition reactions of carbonyl compounds with $NaBH_4$ to form alcohols.
- Be able to outline the mechanism for nucleophilic addition reactions of aldehydes and ketones with $NaBH_4$.

Specification Reference 6.1.2

Reducing aldehydes and ketones

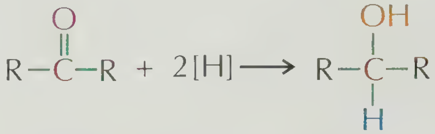
In Module 4: Section 2, you saw how primary alcohols can be oxidised to produce aldehydes and carboxylic acids, and how secondary alcohols can be oxidised to make ketones. Using a reducing agent you can reverse these reactions. $NaBH_4$ (sodium tetrahydridoborate(III) or sodium borohydride) is usually the reducing agent used. But in equations, [H] is often used to indicate a hydrogen from a reducing agent. The equation below shows the reduction of an aldehyde to a primary alcohol:



$$R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}H + 2[H] \longrightarrow R{-}\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}{-}H$$

Exam Tip
When you're writing equations like this in an exam make sure you balance the [H]s as well as the molecules.

And here's the reduction of a ketone to a secondary alcohol:

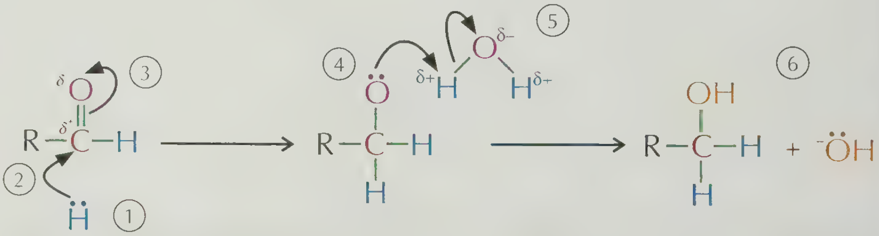


$$R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}R + 2[H] \longrightarrow R{-}\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}{-}R$$

Nucleophilic addition reactions

You need to understand the reaction mechanisms for the reduction of aldehydes and ketones back to alcohols. These are **nucleophilic addition** reactions — an H^- ion from the reducing agent acts as a nucleophile and adds on to the δ^+ carbon atom of a carbonyl group. You haven't covered nucleophilic addition reactions before so here's the mechanism...

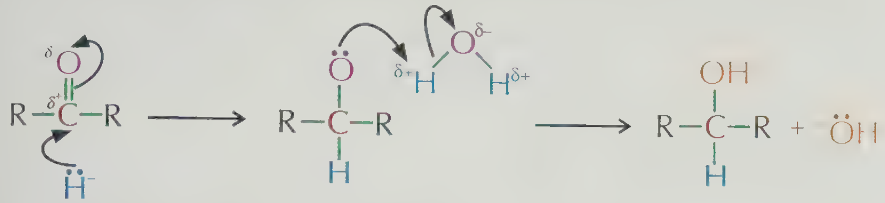
Tip: Remember that a nucleophile is an electron pair donor. They react with atoms with a positive, or partial positive, charge.



1. The C=O bond is polar so the $C^{\delta+}$ attracts the negatively charged lone pair of electrons on the H^- ion.
2. The H^- ion attacks the slightly positive carbon atom and donates its lone pair of electrons, forming a dative covalent bond with the carbon.
3. As carbon can only have 4 bonds, the addition of the H^- ion causes one of the carbon-oxygen bonds to break. This forces a lone pair of electrons from the C=O double bond onto the oxygen.
4. The negatively charged oxygen donates its lone pair of electrons to a $H^{\delta+}$ atom on a water molecule and...
5. ...the electrons from the O–H bond are donated to the $O^{\delta-}$ atom.
6. A primary alcohol and an ^-OH ion are produced.

Exam Tip
You need to be able to draw the mechanism for the reduction of any aldehyde or ketone — so make sure you understand all the steps of these nucleophilic addition reactions.

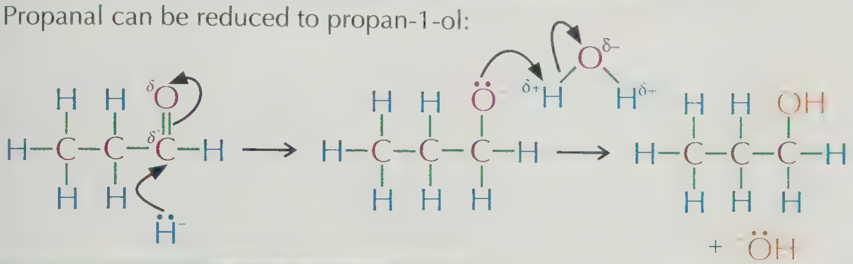
The mechanism for the reduction of a ketone is the same as for an aldehyde — you just get a secondary alcohol at the end instead of a primary alcohol:



This reaction mechanism can be applied to any aldehyde or ketone.

Example

Propanal can be reduced to propan-1-ol:

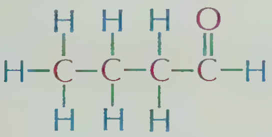


Exam Tip
You must draw the curly arrows coming from the lone pair of electrons, or from a covalent bond. If you don't — you won't get the marks for the mechanism in the exam.

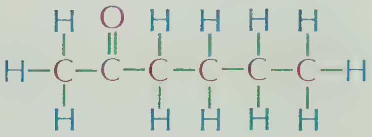
Practice Questions — Application

Q1 For each molecule below, draw the mechanism for its reduction to an alcohol.

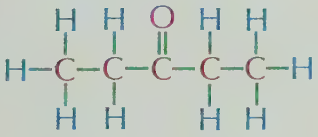
a)



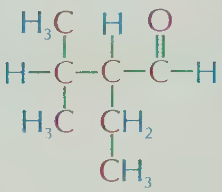
b)



c)



d)



Q2 Write an equation for the reduction of pentan-2-one to pentan-2-ol. Use [H] to represent a reducing agent.

Q3 Write an equation for the reduction of 2-methylhexanal to an alcohol. Use [H] to represent a reducing agent.

Q4 Write an equation for the reduction of pentan-2,4-dione to an alcohol. Use [H] to represent a reducing agent.

Q5 The product of reducing molecule **X** is 2-methylbutan-1,3-diol. Write down the structural formula of molecule **X**.

Tip: Don't forget — aldehydes are reduced to primary alcohols and ketones are reduced to secondary alcohols.

Tip: Remember that all the carbonyl groups in a molecule will be reduced if you add a reducing agent.

Practice Questions — Fact Recall

Q1 Name a reducing agent which could be used to reduce an aldehyde to a primary alcohol.

Q2 Is a secondary alcohol formed by reducing an aldehyde or a ketone?

Q3 Name the reaction mechanism that takes place when ketones are reduced to alcohols.

7. Reactions with Carbonyls

Learning Objectives:

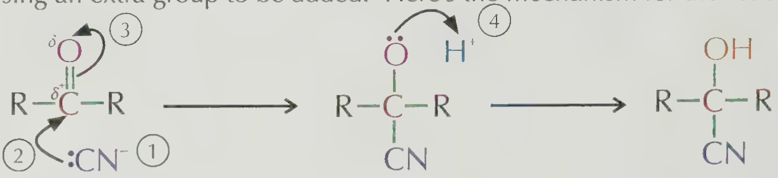
- Be able to describe nucleophilic addition reactions of carbonyl compounds with HCN to form hydroxynitriles.
- Be able to outline the mechanism for nucleophilic addition reactions of aldehydes and ketones with HCN.
- Be able to describe the use of 2,4-dinitrophenyl hydrazine to detect the presence of a carbonyl group in an organic compound, and identify a carbonyl compound from the melting point of the derivative (PAG 7).
- Be able to describe the use of Tollens' reagent to detect the presence of an aldehyde group, and distinguish between aldehydes and ketones, explained in terms of the oxidation of aldehydes to carboxylic acids with reduction of silver ions to silver (PAG 7).

Specification Reference 6.1.2

Using tests to identify unknown compounds is an important skill if you want to be a CSI agent. But it's also pretty useful in the lab when you want to know what you've made — a few tests you've got to know are covered below.

Hydrogen cyanide

Hydrogen cyanide reacts with carbonyl compounds to produce hydroxynitriles (molecules with a CN and OH group). This is another example of a nucleophilic addition reaction — a nucleophile attacks the molecule, causing an extra group to be added. Here's the mechanism for the reaction:

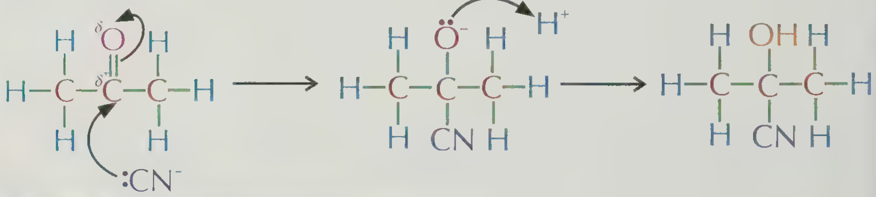


1. Hydrogen cyanide's a weak acid — it partially dissociates in water to form H^+ ions and CN^- ions: $HCN \rightleftharpoons H^+ + CN^-$.
2. The CN^- ion from the HCN attacks the partially positive carbon atom and donates a pair of electrons forming a bond with the carbon.
3. A pair of electrons from the C=O double bond is pushed onto the oxygen.
4. The oxygen bonds to a H^+ ion (from either hydrogen cyanide or water) to form the hydroxyl group (OH) and a hydroxynitrile is produced.

Hydrogen cyanide is very toxic, so this reaction is normally done with acidified sodium cyanide ($NaCN/H^+$), which is less dangerous but still provides the CN^- and H^+ ions required for the reaction (see below).

Example

Propanone and acidified sodium cyanide react to form 2-hydroxy-2-methylpropanenitrile. The mechanism for this reaction is shown below:



Risk assessments

HOW SCIENCE WORKS

A **risk assessment** involves reviewing the hazards of the reacting chemicals, the products and any conditions needed, such as heat. You don't have to wrap yourself in cotton wool, but you do have to take all reasonable precautions to reduce the risk of an accident.

Example

Here's a bit of a risk assessment for reacting hydrogen cyanide with a carbonyl compound:

Hydrogen cyanide (HCN) is an extremely toxic gas. So to reduce the risk, acidified sodium cyanide is used instead. This is also toxic but it can be stored more safely. Acidified sodium cyanide is used for the reaction to supply both the CN^- ions and the H^+ ions needed. However, the reaction should still be done in a fume cupboard as there is still a risk of some HCN gas being released from the solution.

Caution
Toxic Chemicals

***Figure 1:** Warning labels on the bottles of chemicals warn you if a chemical is dangerous.*

Brady's reagent

PRACTICAL ACTIVITY GROUP 7

Brady's reagent is 2,4-dinitrophenylhydrazine (2,4-DNPH) (see Figure 2) dissolved in methanol and concentrated sulfuric acid.

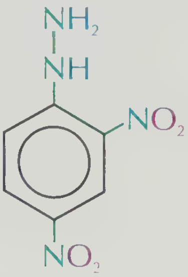


Figure 2: *Brady's reagent (2,4-dinitrophenylhydrazine).*

The 2,4-dinitrophenylhydrazine forms a bright orange precipitate if a carbonyl group is present (see Figure 3). This only happens with C=O groups, not with ones like COOH, so it only tests for aldehydes and ketones.

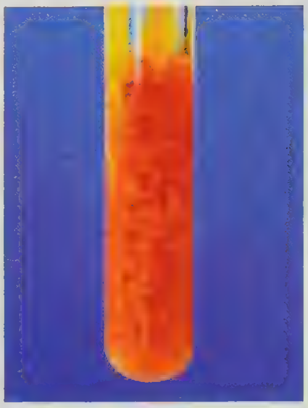


Figure 3: *Brady's reagent reacting with propanone.*

Using melting points to identify unknown carbonyls

The orange precipitate is a derivative of the carbonyl compound. Each different carbonyl compound produces a crystalline derivative with a different melting point. So if you measure the melting point of the crystals and compare it against the known melting points of the derivatives, you can identify the carbonyl compound.

Tip: A derivative of a compound is a similar compound to the original or one that has been made from it.

Example

An unknown carbonyl compound, molecule **J**, is reacted with Brady's reagent and an orange precipitate is formed. The melting point of the product was found to be 115.3 °C. Use the table below to identify molecule **J**.

Carbonyl compound	Melting point of 2,4-DNPH derivative (°C)
Propanal	156
Methylpropanal	182
Butan-2-one	115
3-methylbutan-2-one	124

Butan-2-one has a 2,4-DNPH derivative with a melting point of 115 °C. So molecule **J** must be butan-2-one.

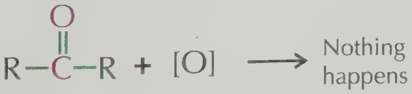
Tip: There's more about how to find the melting point of a substance on page 500.

Tollens' reagent

PRACTICAL ACTIVITY GROUP 7

This test lets you distinguish between an aldehyde and a ketone. It uses the fact that an aldehyde can be easily oxidised to a carboxylic acid, but a ketone can't.

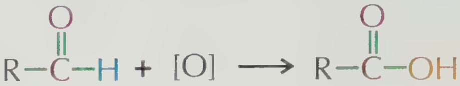
Remember, the only way to oxidise a ketone would be to break a carbon-carbon bond so ketones are not easily oxidised (see pages 450-451).



$$R-\overset{\overset{\large O}{\|}}{C}-R + [O] \longrightarrow \text{Nothing happens}$$

Tip: In these equations [O] is used to represent an oxidising agent.

But aldehydes can be easily oxidised to carboxylic acids because they have a hydrogen attached to the carbonyl group:



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-H + [O] \longrightarrow R-\overset{\overset{\displaystyle O}{\|}}{C}-OH$$

As the aldehyde is oxidised, the oxidising agent is reduced — so a reagent is used that changes colour as it's reduced.

Tollens' reagent is a colourless solution of silver nitrate ($AgNO_3$) dissolved in aqueous ammonia. If it's heated in a test tube with an aldehyde, a silver mirror forms after a few minutes (see Figure 4). As the aldehyde is oxidised the silver ions in the Tollens' reagent are reduced, producing a silver mirror:

Colourless *Silver*

$$Ag^+_{(aq)} + e^- \rightarrow Ag_{(s)}$$

Silver ions in the Tollens' reagent are reduced.

Electrons come from the oxidation of the aldehyde.

The silver produced forms a silver mirror.

As ketones aren't easily oxidised, they won't react with Tollens' reagent — so there'll be no colour change.

Tip: Silver nitrate dissolved in aqueous ammonia is sometimes called ammoniacal silver nitrate.

Tip: Aldehydes and ketones are flammable, so they must be heated in, e.g. a water bath, rather than over a flame. See pages 33 and 34 for more on methods of heating substances without using a naked flame.

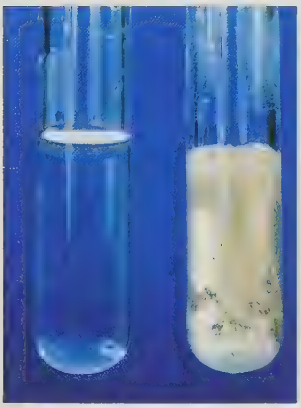
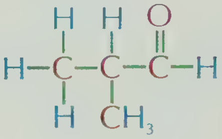


Figure 4: *Tollens' reagent. The test tube on the left shows the unreacted Tollens' reagent. The test tube on the right shows the result of a reaction with an aldehyde.*

Practice Questions — Application

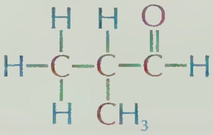
Q1 a) Draw the structure of the hydroxynitrile that would be produced if 2-methylpropanal was reacted with HCN. The structure of 2-methylpropanal is shown below:



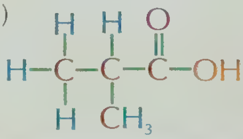
b) Draw the mechanism for this reaction.

Q2 Describe what you would observe if you reacted each of the compounds below with: a) Brady's reagent, b) Tollens' reagent.

i)



ii)



Practice Questions — Fact Recall

Q1 What does Brady's reagent test for?

Q2 Describe how you could use Brady's reagent and melting point data to determine the identity of an unknown compound.

Q3 What is Tollens' reagent?

Q4 Give the formula of the positive ion present in Tollens' reagent.

8. Carboxylic Acids

You've met these crazy compounds before, but here's a bit more detail about them and their reactions.

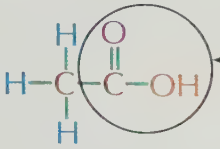
Learning Objectives:

- Be able to explain the water solubility of carboxylic acids in terms of hydrogen bonding.
- Understand the reactions in aqueous conditions of carboxylic acids with metals and bases (including carbonates, metal oxides and alkalis). (PAG 7)

Specification Reference 6.1.3

What are carboxylic acids?

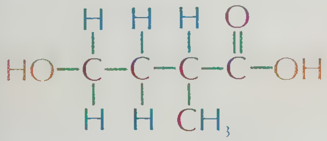
Carboxylic acids contain the carboxyl functional group –COOH.



This is the carboxyl functional group.

To name them, you find and name the longest alkane chain, take off the 'e' and add '–oic acid'. The carboxyl group is always at the end of the molecule and when naming it's more important than other functional groups — so all the other functional groups in the molecule are numbered starting from this carbon.

Example



The longest continuous carbon chain is 4 carbon atoms, so the stem is butane.

Numbering of the carbons starts at the COOH group so there's a COOH group on carbon-1, a methyl group on carbon-2 and a hydroxyl group on carbon-4.

So, this is 4-hydroxy-2-methylbutanoic acid.

Tip: A carboxyl group contains a carbonyl group and a hydroxyl group on the same carbon atom.

Tip: You've already covered how to name carboxylic acids on page 250 so this should just be a recap.

Solubility of carboxylic acids

Carboxylic acids are **polar** molecules, since electrons are drawn from the carbon atoms in the carbonyl groups towards the more **electronegative** oxygen atoms. This makes small carboxylic acids very soluble in water, as they form hydrogen bonds with the water molecules (see Figure 1).

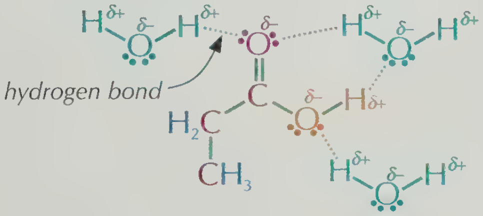
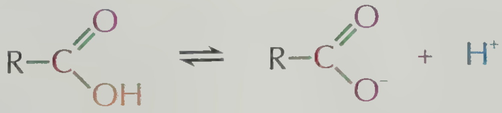


***Figure 1:** Hydrogen bonds between propanoic acid and water molecules.*

Exam Tip
If you're asked to draw hydrogen bonding in an exam don't forget to mark on the lone pairs of electrons and label the hydrogen bond and all the δ+ and δ– atoms.

Dissociation of carboxylic acids

Carboxylic acids are weak acids — in water they partially dissociate into a carboxylate ion and an H^+ ion.



Carboxylic acid *Carboxylate ion*

This reaction is reversible but the equilibrium lies to the left because most of the molecules don't dissociate.

Tip: See page 336 for more on the dissociation of weak acids.

Reaction with metals, carbonates and bases

PRACTICAL ACTIVITY GROUP 7

Carboxylic acids react with the more reactive metals in a redox reaction to form a salt and hydrogen gas.

Example

$2CH_3COOH_{(aq)} + Mg_{(s)} \rightarrow (CH_3COO)_2Mg_{(aq)} + H_{2(g)}$

Ethanoic acid *Magnesium ethanoate*

Carboxylic acids react with carbonates (CO_3^{2-}) to form a salt, carbon dioxide and water.

Example

$2CH_3COOH_{(aq)} + Na_2CO_{3(s)} \rightarrow 2CH_3COONa_{(aq)} + H_2O_{(l)} + CO_{2(g)}$

Ethanoic acid *Sodium carbonate* *Sodium ethanoate*

In reactions between carboxylic acids and metals, and carboxylic acids and carbonates, the gas evolved during the reaction fizzes out of the solution.

Carboxylic acids are neutralised by bases (like metal oxides and hydroxides) to form a salt and water.

Example

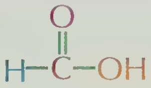
$2CH_3COOH_{(aq)} + MgO_{(s)} \rightarrow (CH_3COO)_2Mg_{(aq)} + H_2O_{(l)}$

Ethanoic acid *Magnesium ethanoate*

Practice Questions — Application

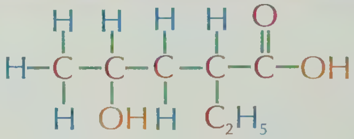
Q1 Below are two carboxylic acids:

(i)



$H-\overset{\overset{O}{\|}}{C}-OH$

(ii)



$H-\underset{H}{\overset{H}{C}}-\underset{OH}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{C_2H_5}{\overset{H}{C}}-\overset{\overset{O}{\|}}{C}-OH$

a) Name these carboxylic acids.

b) Write a balanced equation for the reaction of carboxylic acid (i) with magnesium metal.

c) Write a balanced equation for the reaction of carboxylic acid (ii) with sodium carbonate (Na_2CO_3).

Q2 Write a balanced equation for the reaction between 2-methylbutanoic acid and $NaOH_{(aq)}$.

Practice Questions — Fact Recall

Q1 Write down the functional group of carboxylic acids.

Q2 Explain why small carboxylic acids, like ethanoic acid, are highly soluble in water. Draw a diagram to help you explain your answer.

Q3 Describe what you would observe if a carboxylic acid reacted with magnesium metal.

Tip: Salts of carboxylic acids are called carboxylates and their names end with –oate.

Figure 2: Calcium carbonate reacting with ethanoic acid. The reaction gives off bubbles of carbon dioxide.

Tip: Simple carboxylic acids form 1– ions (e.g. CH_3COO^-). So you need one molecule to react with a 1+ ion (like sodium), but two to react with a 2+ ion (like magnesium).

Exam Tip
When you're naming molecules in the exam, check your spelling. You'll lose marks even if there's only one letter out of place.

Tip: Remember to double check that your equations balance when you've finished.

9. Acyl Chlorides

Acyl chlorides are a particularly useful type of carbonyl compound because they are good starting points for making lots of different types of molecule.

Learning Objectives:

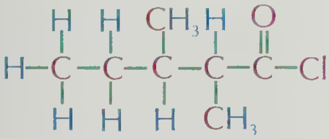
- Be able to explain the formation of acyl chlorides from carboxylic acids using $SOCl_2$.
- Understand the use of acyl chlorides in synthesis in formation of esters, carboxylic acids and primary and secondary amides.

Specification Reference 6.1.3

What are acyl chlorides?

Acyl (or acid) chlorides have the functional group COCl — their general formula is $C_nH_{2n-1}OCl$. Naming acyl chlorides is similar to naming carboxylic acids. All their names end in –oyl chloride and the carbon atoms are numbered from the end with the acyl functional group.

Example



2,3-dimethylpentanoyl chloride

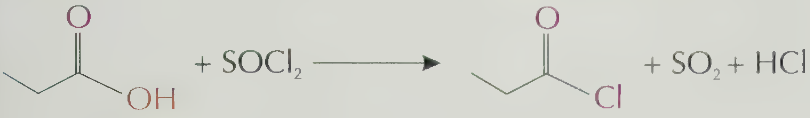
The longest continuous carbon chain is 5 carbon atoms, so the stem is pentane.

There are methyl groups on carbon-2 and carbon-3.

So, it's 2,3-dimethylpentanoyl chloride.

They're made by reacting carboxylic acids with $SOCl_2$ (thionyl chloride) — the –OH group in the acid is replaced by –Cl.

Example



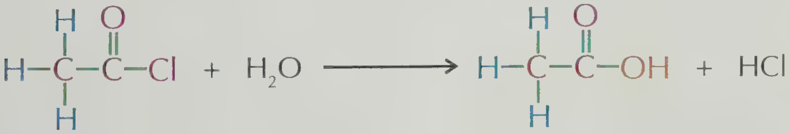
propanoic acid *propanoyl chloride*

Reactions of acyl chlorides

Acyl chlorides can react with a wide range of different molecules. In each of these reactions, Cl is substituted by an oxygen or nitrogen group — they're nucleophilic substitution reactions:

Reaction with water

Acyl chlorides react vigorously with cold water, producing a carboxylic acid.

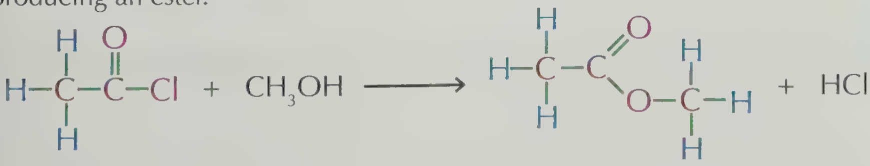


Ethanoyl chloride *Ethanoic acid*

Figure 1: *The reaction of an acyl chloride with water. You can see the misty fumes of HCl that are being given off.*

Reaction with alcohols

Acyl chlorides react vigorously with alcohols at room temperature, producing an ester.

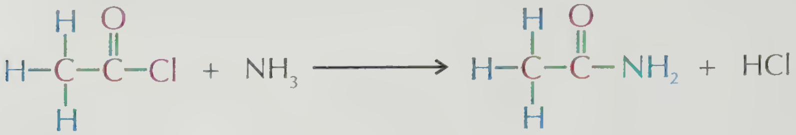


Ethanoyl chloride *Methanol* *Methyl ethanoate*

This irreversible reaction is a much easier, faster way to produce an ester than esterification (see page 462).

Reaction with ammonia

Acyl chlorides react violently with ammonia at room temperature, producing a **primary amide**.

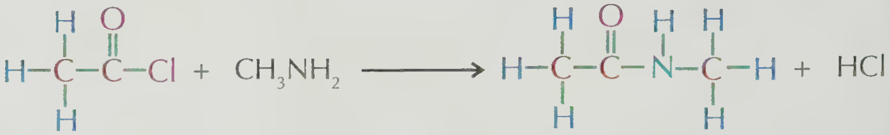


Ethanoyl chloride *Ethanamide*

Tip: If you carried out this reaction in the lab, you'd actually get a mixture of ethanamide, hydrochloric acid and ammonium chloride. This is because, once it's produced, the hydrochloric acid product reacts with the ammonia reactant:
$CH_3COCl + 2NH_3 \rightarrow CH_3CONH_2 + NH_4Cl$

Reaction with amines

Acyl chlorides react violently with **amines** at room temperature, producing a **secondary amide**.

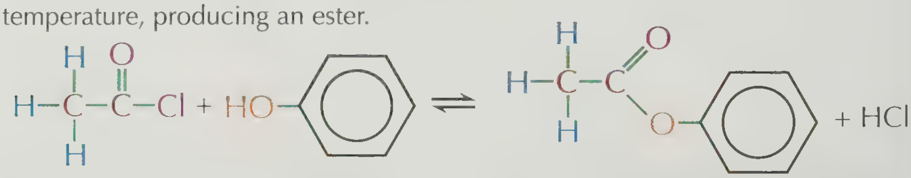


Ethanoyl chloride *Methylamine* *N-methylethanamide*

Tip: See pages 469-472 for more on amines and amides.

Reaction with phenol

Acyl chlorides react slowly with phenol at room temperature, producing an ester.



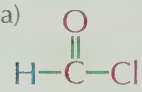
Ethanoyl chloride *Phenol* *Phenyl ethanoate*

You can normally make esters by reacting an alcohol with a carboxylic acid. Phenols react very slowly with carboxylic acids, so it's faster to use an acyl chloride.

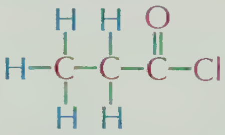
Practice Questions — Application

Q1 Name the acyl chlorides that are shown below:

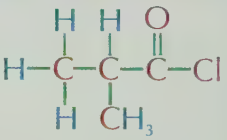
(a)



(b)



(c)



Q2 Write out the equations for the following reactions of the compounds in question 1:

a) The acyl chloride in Q1a with methanol.

b) The acyl chloride in Q1b with water.

c) The acyl chloride in Q1c with ammonia.

Practice Questions — Fact Recall

Q1 What is the general formula for an acyl chloride?

Q2 Write out a reaction for making ethanoyl chloride from ethanoic acid.

Q3 What are the products when an acyl chloride is reacted with:

a) water? b) an alcohol? c) ammonia? d) an amine?

10. Esters

Esters are another type of compound that contains a carbonyl group, and they have a few reactions and properties you have to learn for your exams.

Naming esters

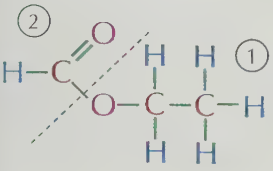
An **ester** is formed by reacting an alcohol with a carboxylic acid or a carboxylic acid derivative (see next page). So the name of an ester is made up of two parts — the first bit comes from the alcohol, and the second bit from the carboxylic acid (or its derivative).

To name an ester, just follow these steps:

1. Look at the alkyl group that came from the alcohol.
   This is the first bit of the ester's name.
2. Now look at the part that came from the carboxylic acid.
   Swap its '-oic acid' ending for 'oate' to get the second bit of the name.
3. Put the two parts together.

Example

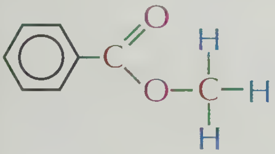
Methanoic acid reacts with ethanol to produce the ester shown below:



1. This part of the ester came from the alcohol. It's an ethyl group, so the first part of the ester's name is ethyl-.
2. This part of the ester came from the carboxylic acid. It was methanoic acid, so the second part of the ester's name is -methanoate.
3. So this ester is ethyl methanoate.

The same rules apply even if the carbon chains are branched or if the molecule has a benzene ring attached. Always number the carbons starting from the carbon atoms in the C–O–C bond.

Examples

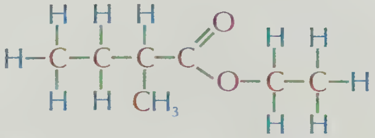


This ester has a methyl group that came from the alcohol so the name begins with methyl-.

There is a benzene ring that came from benzoic acid so the name ends in -benzoate.

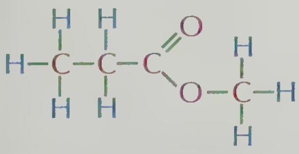
So this is methyl benzoate.

This ester has an ethyl group that came from the alcohol and the carboxylic acid part was 2-methylbutanoic acid, so it is called ethyl 2-methylbutanoate.



Sometimes you may be asked to predict which alcohol and which carboxylic acid are needed to form a particular ester.

Example



There are 3 carbons in the part of the molecule that came from the acid so the stem is propane. This part came from propanoic acid.

There is one carbon in the section that came from the alcohol so the stem is methane. This part of the molecule came from methanol.

Learning Objectives:

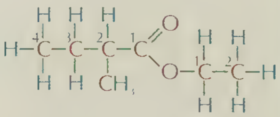
- Be able to describe the esterification of carboxylic acids with alcohols in the presence of an acid catalyst.
- Be able to describe the esterification of acid anhydrides with alcohols.
- Be able to describe the hydrolysis of esters in hot aqueous acid to form carboxylic acids and alcohols.
- Be able to describe the hydrolysis of esters in hot aqueous alkali to form carboxylate salts and alcohols.

Specification Reference 6.1.3

Tip: A carboxylic acid derivative is just something that can be made from a carboxylic acid — like an acyl chloride.

Tip: Be careful — the name of the ester is written the opposite way round to the formula.

Tip: Here's how you'd number the carbons in ethyl 2-methylbutanoate:

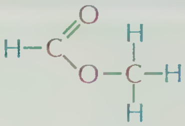


It doesn't matter that there are two C_1s (and C_2s) because one's in the bit that came from the alcohol and the other's in the bit from the acid.

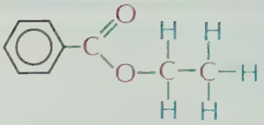
Practice Question — Application

Q1 Two esters are shown on the right:

(i)



(ii)



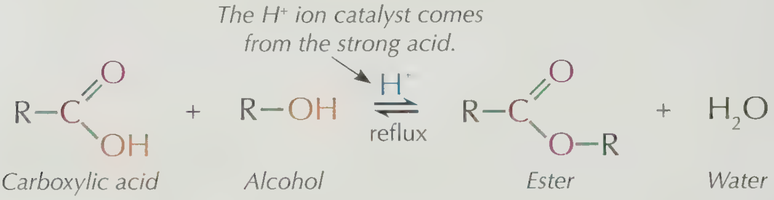
a) Name these esters

b) State a carboxylic acid and an alcohol that could have reacted to form each of these esters.

Producing esters

Producing esters using alcohols and carboxylic acids

If you heat a carboxylic acid with an alcohol in the presence of a strong acid catalyst, you get an ester. It's called an **esterification** reaction.



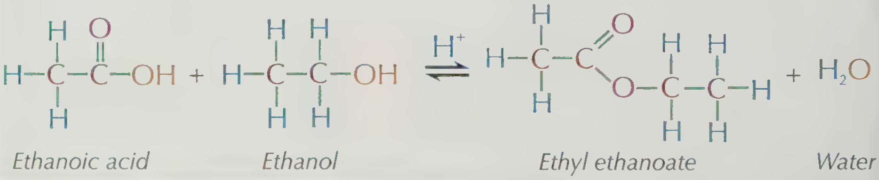
The H^+ ion catalyst comes from the strong acid.

Tip: This reaction is also a condensation reaction — molecules are combining by releasing a small molecule (e.g. water).

Concentrated sulfuric acid (H_2SO_4) is usually used as the acid catalyst but other strong acids such as HCl or H_3PO_4 can also be used.

Example

Ethanoic acid reacts with ethanol to produce ethyl ethanoate and water.



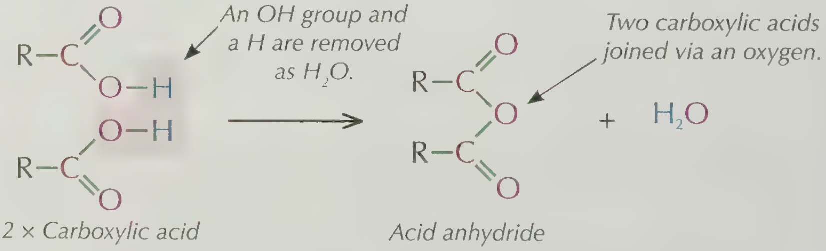
Exam Tip
These reactions are reversible, so don't forget the forwards-backwards arrows (⇌) when you're writing these equations in the exam.

The reaction is reversible, so you need to separate out the product as it forms. Small esters are very volatile, so for them you can just warm the mixture and distil off the ester. Large esters are harder to form so it's best to heat them under reflux and use distillation to separate the ester from the other compounds.

Tip: If you can't remember what distillation or refluxing apparatus look like have a look at page 498.

Producing esters from alcohols and acid anhydrides

An **acid anhydride** is made from two identical carboxylic acid molecules. The two carboxylic acid molecules are joined together via an oxygen with the carbonyl groups on either side. Acid anhydride formation is shown below.



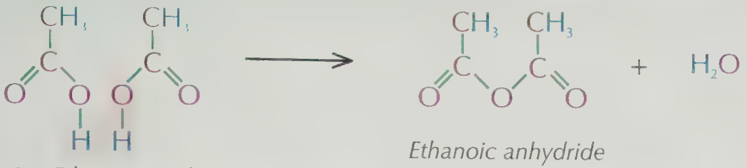
An OH group and a H are removed as H_2O.

Two carboxylic acids joined via an oxygen.

If you know the name of the carboxylic acid, acid anhydrides are easy to name — just take away 'acid' and add 'anhydride'. So methanoic acid gives methanoic anhydride, ethanoic acid gives ethanoic anhydride, etc.

Tip: At first glance acid anhydrides can seem a bit daunting, but when you realise that they're just two carboxylic acids stuck together they don't look quite so bad.

Example

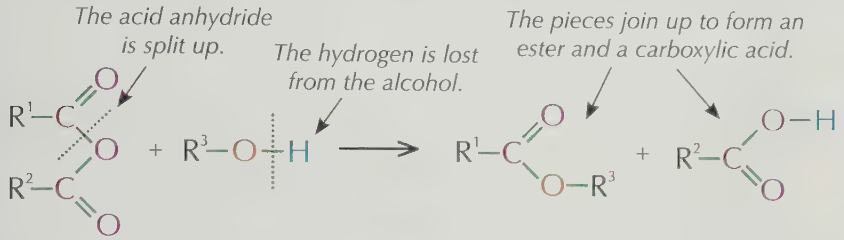


2 × Ethanoic acid

Ethanoic anhydride

Tip: You can also produce esters from alcohols and acyl chlorides — see page 459 for this reaction.

Acid anhydrides can react with alcohols to make esters too. The acid anhydride is warmed with the alcohol. No catalyst is needed. The products are an ester and a carboxylic acid which can then be separated by distillation.


The acid anhydride is split up.

The hydrogen is lost from the alcohol.

The pieces join up to form an ester and a carboxylic acid.

Acid anhydride

Alcohol

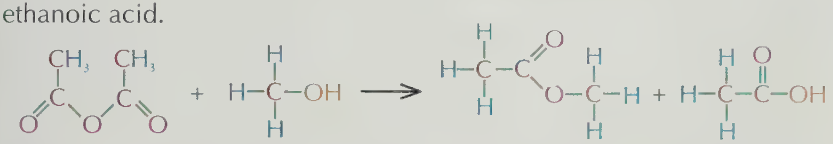
Ester

Carboxylic acid

Tip: This way of making esters is simpler as the reaction isn't reversible — so you can just collect and separate the products at the end of the reaction. However, esters aren't generally produced on an industrial scale in this way as acid anhydrides are expensive.

Example

Ethanoic anhydride reacts with methanol to form methyl ethanoate and ethanoic acid.



Ethanoic anhydride

Methanol

Methyl ethanoate

Ethanoic acid

Practice Questions — Application

Q1 Write an equation to show the formation of propyl pentanoate from an acid and an alcohol.

Q2 Write an equation to show the formation of butyl methanoate and methanoic acid from an acid anhydride and an alcohol.

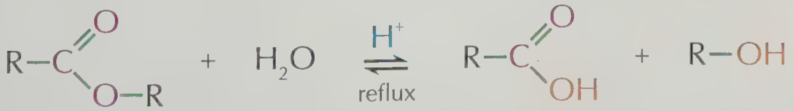
Tip: Yes, I know... Learning the reactions of acid anhydrides is hard. The only thing to do is practise, practise, practise until you can do them standing on your head. Hard work never killed anyone (apart from my aunt Sally — but that's another story).

Hydrolysis of esters

Hydrolysis is when a substance is split up by water — but using just water can be very slow, so an acid or an alkali is often added to speed it up. There are two types of hydrolysis of esters — acid hydrolysis and base hydrolysis. With both types you get an alcohol, but the second product in each case is different.

Acid hydrolysis

Acid hydrolysis splits the ester into an acid and an alcohol — it's the reverse of the reaction on page 462. You have to heat the ester under reflux with a dilute acid, such as hydrochloric or sulfuric. The ester will then split back into the carboxylic acid and alcohol it was originally made from.



Ester

Water

Carboxylic acid

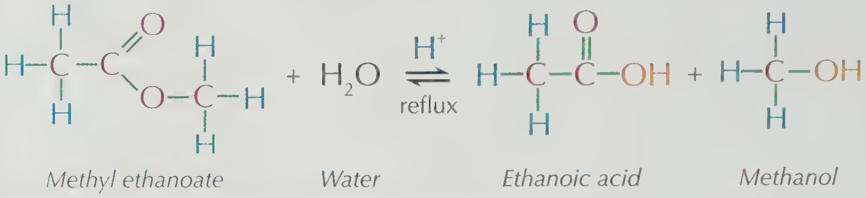
Alcohol

Tip: Hydrolysis comes from two Greek words — 'hydro' meaning water and 'lysis' meaning to separate. So hydrolysis means separation using water. Simple.

Figure 1: A molecular model of methanol.

Example

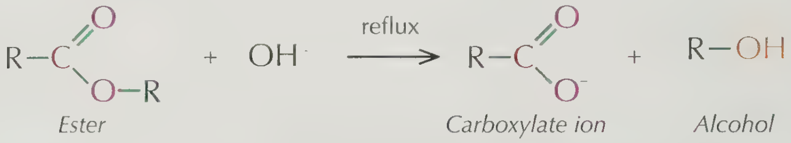
Acid hydrolysis of methyl ethanoate produces ethanoic acid and methanol:


+ H_2O
H^+
reflux
Methyl ethanoate
Water
Ethanoic acid
Methanol

As these acid hydrolysis reactions are reversible you need to use lots of water to push the equilibrium over to the right so you get lots of product. See pages 321-333 for more on reversible reactions and equilibria.

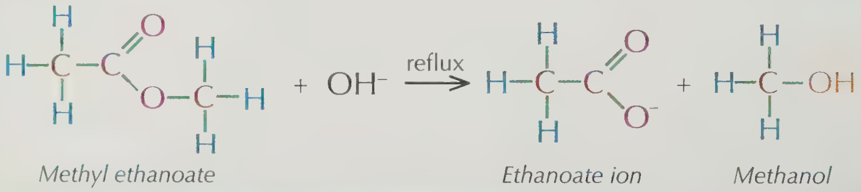
Base hydrolysis

For a base hydrolysis reaction you have to reflux the ester with a dilute alkali, such as sodium hydroxide. When heated, OH^- ions from the base react with the ester and you get a carboxylate salt and an alcohol.

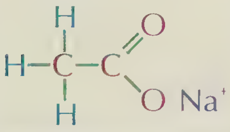

+ OH^-
reflux
+
R–OH
Ester
Carboxylate ion
Alcohol

Example

Base hydrolysis of methyl ethanoate produces ethanoate ions and methanol:


+ OH^-
reflux
+
Methyl ethanoate
Ethanoate ion
Methanol

Tip: The carboxylate ion will form a salt with the positive ion from the alkali. For example, in this reaction sodium ethanoate would be formed if the alkali used was sodium hydroxide:



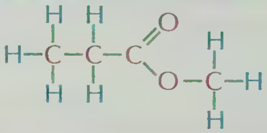
Practice Question — Application

Q1 To the right is the ester methyl propanoate:

Write an equation to show:

a) the acid hydrolysis of this ester,

b) the base hydrolysis of this ester.



Practice Question — Fact Recall

Q1 What two products are produced when an ester is broken down by:

a) acid hydrolysis?

b) base hydrolysis?

Section Summary

Make sure you know...

- The Kekulé and delocalised models of benzene.
- The evidence that supports the delocalised model of benzene, including its bond lengths, its enthalpy change of hydrogenation and its stability (resistance to reaction).
- How to name aromatic compounds.
- Why it's difficult to get benzene to react with bromine, compared to other alkenes.
- The mechanism for the electrophilic substitution of arenes with a halogen.
- The mechanism for the electrophilic substitution of arenes with nitric acid.
- That Friedel-Crafts reactions add acyl or alkyl groups onto benzene rings.
- What phenols are and how to name them.
- That phenol will react with bases (but not carbonates) to form salts.
- Why phenol reacts more easily with bromine than benzene does.
- How phenol reacts with bromine to form 2,4,6-tribromophenol.
- How phenol reacts with dilute nitric acid to form 2-nitrophenol.
- That an electron-donating group on a benzene ring makes electrophiles more likely to react with carbons 2, 4 and 6.
- That an electron-withdrawing group on a benzene ring makes electrophiles more likely to react with carbons 3 and 5.
- How to predict the substitution products of aromatic compounds by directing effects
- That you can oxidise alcohols using acidified potassium dichromate(VI) ($K_2Cr_2O_7/H_2SO_4$).
- That you can reduce aldehydes and ketones to alcohols using $NaBH_4$.
- The mechanism for the nucleophilic addition reaction of an aldehyde or a ketone with $NaBH_4$.
- How hydroxynitriles can be formed by nucleophilic addition reactions of carbonyl compounds with HCN.
- The mechanism for nucleophilic addition reactions of aldehydes and ketones with HCN.
- That you can use Brady's reagent (2,4-dinitrophenylhydrazine) to test for a carbonyl group.
- How to use Brady's reagent to identify a carbonyl compound from the melting point of the derivative.
- That you can use Tollens' reagent to distinguish between aldehydes and ketones.
- What carboxylic acids are and how to name them.
- That carboxylic acids are soluble in water because they form hydrogen bonds with water molecules.
- The reactions of carboxylic acids with metals, carbonates and bases.
- How acyl chlorides are formed from carboxylic acids using $SOCl_2$.
- How acyl chlorides are used in the synthesis of esters, carboxylic acids and primary and secondary amides.
- What esters are and how to name them.
- How to make esters using carboxylic acids and alcohols or acid anhydrides and alcohols.
- The reactions for the acid and base hydrolysis of esters.

Exam-style Questions

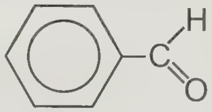
1 The longest carbon chain in a carboxylic acid is 4 carbons long. What is the maximum number of carbons that it could have?

- **A** 4
- **B** 6
- **C** 8
- **D** 10

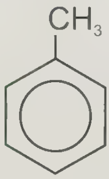
(1 mark)

2 Which of the following could not have been the result of a Friedel-Crafts reaction?

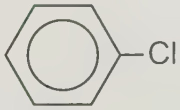
A



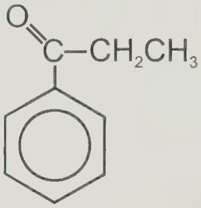
B



C



D



(1 mark)

3 Esterification is the formation of an ester by reacting a carboxylic acid and an alcohol in the presence of a catalyst. Which of the following would be a suitable catalyst for this reaction?

- **A** Dilute H_2SO_4
- **B** Concentrated NaOH
- **C** Dilute NH_3
- **D** Concentrated H_3PO_4

(1 mark)

4 Phenol is reacted with iodine. Which of the following is the most likely product as a result of this reaction?

A 2-iodophenol

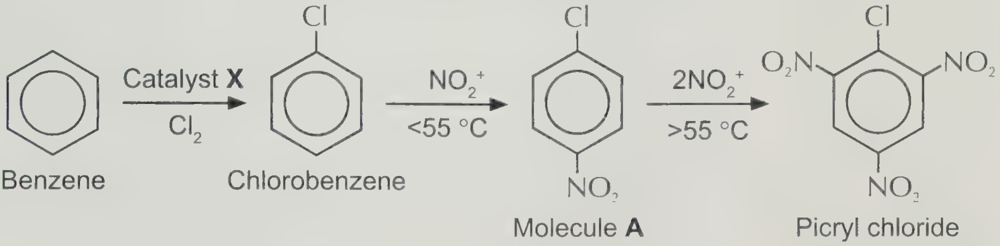
B 3-iodophenol

C 5-iodophenol

D 6-iodophenol

(1 mark)

5 A scientist is trying to synthesise the explosive picryl chloride (1-chloro-2,4,6-trinitrobenzene) from benzene. The synthesis route used by the scientist is shown below.



(a) (i) Give the catalyst (Catalyst **X**) required to produce chlorobenzene from benzene.

(1 mark)

(ii) Describe the role of Catalyst **X** in the reaction between benzene and Cl_2.

(3 marks)

(b) (i) Write an equation for the production of the NO_2^+ ion in the second step of this synthesis.

(1 mark)

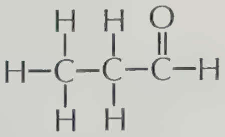
(ii) Draw the mechanism for the reaction of NO_2^+ with chlorobenzene to produce Molecule **A**.

(4 marks)

(iii) Name Molecule **A**.

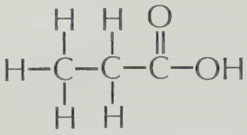
(1 mark)

6 The following molecules are all derived from propane.



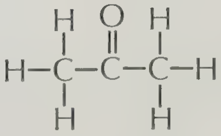
$$\begin{array}{ccccccc} & & H & & H & & O \\ & & | & & | & & \| \\ H & - & C & - & C & - & C & - & H \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

Molecule **X**



$$\begin{array}{ccccccc} & & H & & H & & O \\ & & | & & | & & \| \\ H & - & C & - & C & - & C & - & OH \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

Molecule **Y**



$$\begin{array}{ccccccc} & & H & & O & & H \\ & & | & & \| & & | \\ H & - & C & - & C & - & C & - & H \\ & & | & & & & | \\ & & H & & & & H \end{array}$$

Molecule **Z**

(a) Name molecules **X**, **Y** and **Z**.

(3 marks)

(b) Molecule **Z** can be reduced to an alcohol using a hydride ion.

(i) Give a reducing agent that you could use for this reaction.

(1 mark)

(ii) Draw the mechanism for the reaction of Molecule **Z** with H^-.

(4 marks)

(iii) Write the equation for this reaction using [H] to represent the reducing agent.

(2 marks)

(c) Molecule **Y** is a carboxylic acid.

(i) Explain why Molecule **Y** is soluble in water.

(2 marks)

(ii) Write an equation for the reaction of molecule **Y** with sodium carbonate (Na_2CO_3).

(2 marks)

(d) State the reagents needed to produce molecule **X** from propan-1-ol.

(1 mark)

(e) Compounds **X**, **Y** and **Z** are treated with Brady's reagent and Tollens' reagent.

Explain how you could distinguish between molecules **X**, **Y** and **Z** using the results of these reactions.

(3 marks)

7 2-methylpropanoic acid is a carboxylic acid.

(a) Draw the structure of this carboxylic acid.

(1 mark)

(b) Carboxylic acids react with alcohols to form esters.

(i) Draw the structure of the ester that would be formed if 2-methylpropanoic acid reacted with methanol.

(1 mark)

(ii) Give the IUPAC name for this ester.

(1 mark)

(iii) Suggest a suitable catalyst for this reaction.

(1 mark)

(iv) Write an equation for the hydrolysis of this ester with dilute alkali. Show the structure of the reactants and products in your answer.

(2 marks)

Module 6

Section 2: Nitrogen Compounds and Polymers

1. Amines and Amides

Well, two new functional groups — I bet you're dizzy with excitement. Amines and amides are organic compounds that contain nitrogen atoms. This topic will tell you all about them...

What are amines?

If one or more of the hydrogens in ammonia (NH_3) is replaced with an organic group, you get an **amine**. If one hydrogen is replaced with an organic group, you get a primary amine — if two are replaced, it's a secondary amine, three means it's a tertiary amine and if a fourth organic group is added, it's called a quaternary ammonium ion (see Figure 1).

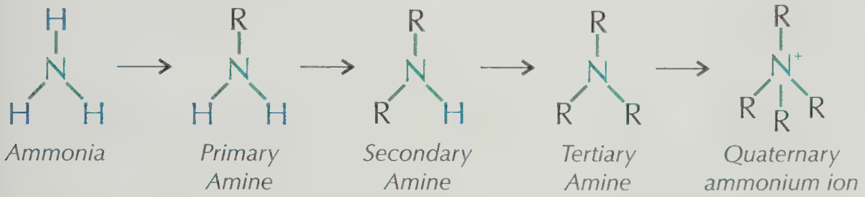
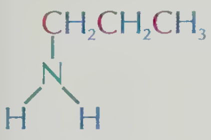


Figure 1: *Diagram showing the different types of amine.*

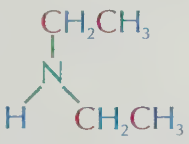
Naming amines

Naming amines is similar to naming other organic compounds. The suffix is -amine (or -amine ion if it's a quaternary ammonium ion). The prefix depends on what organic groups are attached. If the organic groups are all the same you also need to add di- for secondary amines, tri- for tertiary amines and tetra- for quaternary ammonium ions.

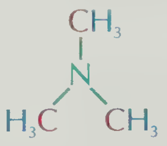
Examples



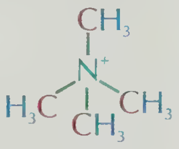
Propylamine



Diethylamine



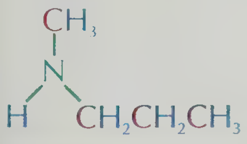
Trimethylamine



Tetramethylamine ion

If the amine has more than one type of organic group attached, you list the different groups in alphabetical order.

Example



This is a secondary amine. It has a methyl group and a propyl group attached.

So this is methylpropylamine.

The basicity of amines

In amines, the lone pair of electrons on the nitrogen atom can form a dative (coordinate) bond with an H^+ ion — the amine donates its lone pair of electrons and 'accepts' the proton (see Figure 2).

Learning Objectives:

- Be able to explain the basicity of amines in terms of proton acceptance by the nitrogen lone pair.
- Know that amines react with dilute acids, e.g. $HCl_{(aq)}$, to form salts.
- Be able to describe the preparation of aliphatic amines by substitution of haloalkanes with excess ethanolic ammonia and amines.
- Be able to describe the preparation of aromatic amines by reduction of nitroarenes using tin and concentrated hydrochloric acid.
- Be able to recognise structures of primary and secondary amides.

Specification Reference 6.2.1, 6.2.2

Tip: If you need a reminder on the basic rules of how to name organic compounds, have a look back at pages 211-212.

Tip: Amines can also be named using the prefix 'amino-'. So aminopropane is the same molecule as propylamine.

Tip: Basicity is a measure of how good a base a compound is.

Exam Tip
If you're asked to draw a species that has a charge, don't forget to put the species in brackets and add the charge.

Dative bonds are covalent bonds where both electrons have come from the same atom.

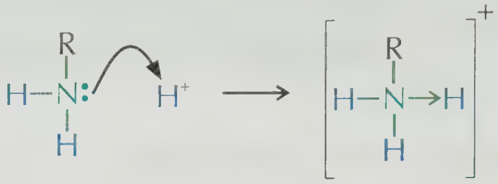


Figure 2: Formation of a dative bond between a primary amine and an H⁺ ion.

Bases can be defined as proton acceptors or electron donors. An amine can accept a proton (H⁺ ion) by donating its lone pair of electrons — so amines are bases.

Figure 3: A student testing an amine solution using litmus paper. The paper has turned blue, showing that the solution is alkaline.

Amine salts

Amines are neutralised by acids to make ammonium salts.

Examples

Methylamine reacts with hydrochloric acid to form methylammonium chloride:

$$\mathbf{CH_3NH_2 + HCl \rightarrow CH_3NH_3^+Cl^-}$$

Ethylamine reacts with sulfuric acid to form diethylammonium sulfate:

$$\mathbf{2CH_3CH_2NH_2 + H_2SO_4 \rightarrow (CH_3CH_2NH_3^+)_2SO_4^{2-}}$$

Tip: Aliphatic amines are amines without a benzene ring. Amines with a benzene ring are called aromatic amines.

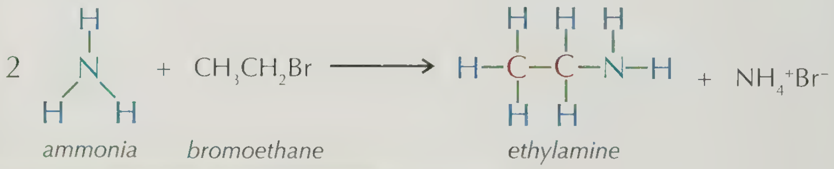
Producing amines

Producing aliphatic amines from haloalkanes

Amines can be made by heating a haloalkane with an excess of ethanolic ammonia (that's just ammonia dissolved in ethanol).

Example

Ethylamine can be produced by heating bromoethane with ammonia:

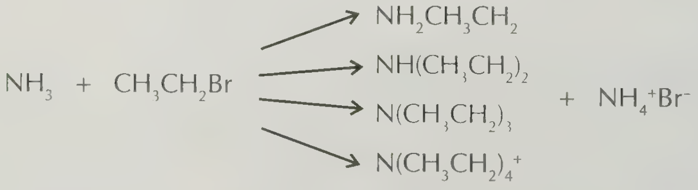


Tip: Producing an amine from a haloalkane and ammonia is an example of a nucleophilic substitution reaction.

But things aren't that simple. You'll actually get a mixture of primary, secondary and tertiary amines, and quaternary ammonium salts, as more than one hydrogen is likely to be substituted.

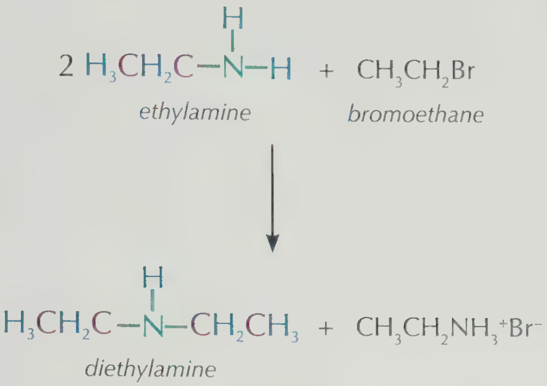
Example

When producing ethylamine you'll actually get a mixture of ethylamine, diethylamine, triethylamine and tetraethylamine ions:



Tip: If you use an excess of ammonia, the bromoethane molecules are more likely to bump into ammonia molecules than secondary or tertiary amines, so you'll increase the yield of the primary amine.
If you use an excess of bromoethane, the reverse is true and you'll increase the yield of the quaternary ammonium ions.

This is because bromoethane can react with ethylamine to form diethylamine:



$$2\,H_3CH_2C{-}\overset{H}{\overset{|}{N}}{-}H + CH_3CH_2Br \longrightarrow H_3CH_2C{-}\overset{H}{\overset{|}{N}}{-}CH_2CH_3 + CH_3CH_2NH_3^+Br^-$$

Tip: As long as the nitrogen atom has a lone pair of electrons, it can go on to react again.

Diethylamine can also react with bromoethane to form triethylamine, and so on...

You can separate the products using distillation if you're trying to make one particular amine.

Producing aromatic amines by reducing a nitro compound

Aromatic amines are produced by reducing an aromatic nitro compound, such as nitrobenzene. There are two steps to the method:

- First you need to heat a mixture of a nitro compound, tin metal and concentrated hydrochloric acid under reflux — this makes an aromatic ammonium salt.
- Then to turn the salt into an aromatic amine, you need to add an alkali, such as sodium hydroxide solution.

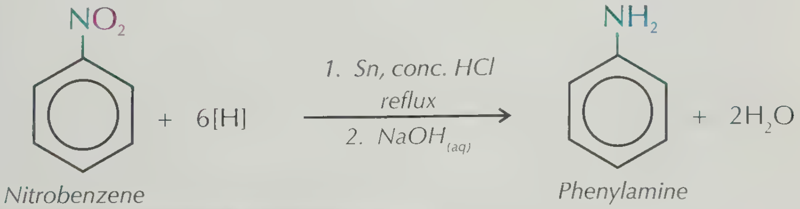
Tip: You saw how to make nitrobenzene from benzene on page 442.

Example

Phenylamine can be made by reducing nitrobenzene:

- Mixing nitrobenzene with tin (Sn) and concentrated HCl and heating under reflux produces the salt $C_6H_5NH_3^+\,Cl^-$.
- Adding NaOH to this salt then releases phenylamine.

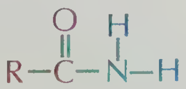
Here's the overall equation for the reaction:



Tip: The [H] in the equation represents the reducing agent (which is the Sn/HCl mixture here).

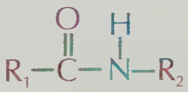
Amides

Amides are carboxylic acid derivatives. They contain the functional group $-CONH_2$. The carbonyl group pulls electrons away from the rest of the $-CONH_2$ group, so amides behave differently from amines. You get primary and secondary amides depending on how many carbon atoms the nitrogen is bonded to.



$$R{-}\overset{O}{\overset{\|}{C}}{-}\overset{H}{\overset{|}{N}}{-}H$$

primary amide



$$R_1{-}\overset{O}{\overset{\|}{C}}{-}\overset{H}{\overset{|}{N}}{-}R_2$$

secondary amide

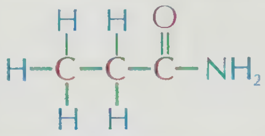
Tip: In the secondary amide, one of the hydrogens attached to the nitrogen is replaced by an alkyl group.

Naming amides

Amides all have the suffix -amide. If the molecule is a primary amide, then the name is simply the stem of the carbon chain, followed by -amide.

Tip: When numbering the main carbon chain in amides, the -CON- carbon is always carbon-1.

Example

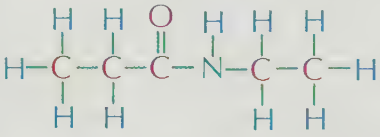


The molecule is a primary amide so the suffix is -amide. The main carbon chain (the longest chain that contains the carbonyl carbon) is three carbon atoms long, so the molecule is propanamide.

Secondary amides also have a prefix to describe the alkyl chain that is attached directly to the nitrogen atom. The prefix has the general form N-alkyl-.

Tip: The N- at the start of the names of secondary amides tells you that the alkyl group is attached to the nitrogen atom.

Example



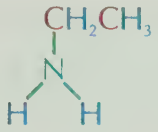
The molecule is a secondary amide so the suffix is -amide. The main carbon chain is three carbon atoms long, so the name of the molecule is based on propanamide. The alkyl group attached to the nitrogen atom is two carbon atoms long, so it's N-ethylpropanamide.

Tip: Don't forget that you list alkyl groups in alphabetical order when you're naming molecules. (You can ignore the effect of any di's or tri's at the front though.)

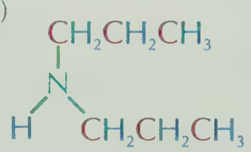
Practice Questions — Application

Q1 Name these amines:

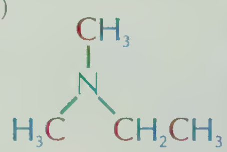
a)



b)



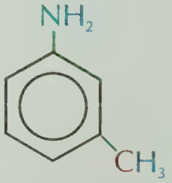
c)



Q2 Write an equation for the reaction between trimethylamine ($N(CH_3)_3$) and hydrochloric acid.

Q3 Write an equation to show the formation of methylamine from chloromethane.

Q4 Write an equation to show the formation of 3-methylphenylamine from 3-methylnitrobenzene. The structure of 3-methylphenylamine is shown on the right.



Practice Questions — Fact Recall

Q1 What is a tertiary amine?

Q2 Explain why amines can act as bases.

Q3 a) How can an amine be produced from a haloalkane?

b) Explain why a mixture of primary, secondary, tertiary and quaternary amines are produced in these reactions.

Q4 Describe how aromatic amines can be produced.

Q5 What is the functional group of a primary amide?

2. Amino Acids

Amino acids contain both an amine group and a carboxylic acid group. This leads to them having some interesting properties and reactions, as they can act as both acids and bases.

What are amino acids?

An **amino acid** has two functional groups — an amine group (NH_2) and a carboxyl group (COOH). There are a few different types of amino acid, but at A-level you only need to know about **α-amino acids**. α-amino acids have both groups attached to the same carbon atom — the 'α carbon'. The general formula of an α-amino acid is $RCH(NH_2)COOH$, where R is an alkyl side-chain which varies from one α-amino acid to the next. The general structure of an α-amino acid is given in Figure 1.

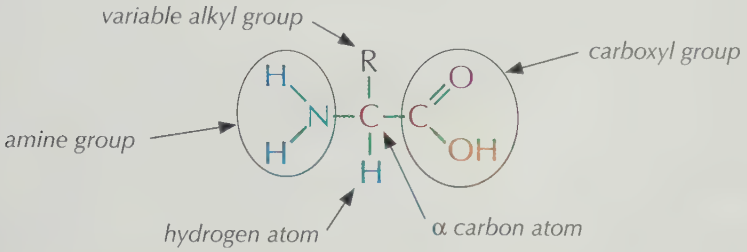


Figure 1: *The general structure of an amino acid.*

Reactions with acids and alkalis

Amino acids contain both an acidic carboxylic acid and a basic amine group. This means they can react with both acids and alkalis to form salts.

- The carboxylic acid group in an amino acid can react with an alkali to form a conjugate base — $RCH(NH_2)COO^-$. This can combine with a positive ion to form a salt. The general equation for this reaction using NaOH is:

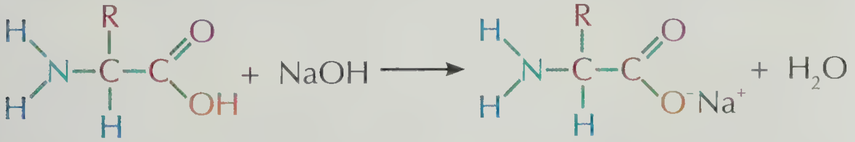
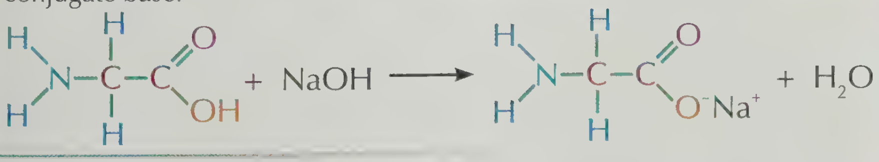


Figure 3: *The reaction of an amino acid with NaOH to form its conjugate base.*

Example

Aminoethanoic acid will react with sodium hydroxide to form the salt of its conjugate base:



- Meanwhile, the amine group can react with an acid to form a salt of the conjugate acid. The general equation for this reaction using HCl is:

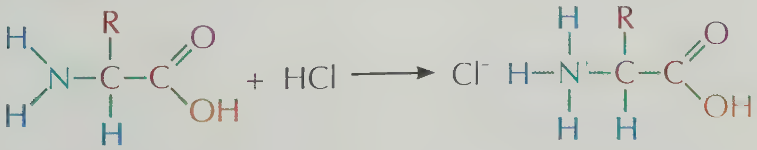


Figure 4: *The reaction of an amino acid with HCl to form its conjugate acid.*

Learning Objectives:

- Know that the general formula for an α-amino acid is $RCH(NH_2)COOH$.
- Be able to describe the reactions of the carboxylic acid group in amino acids with alkalis and in the formation of esters.
- Be able to describe the reaction of the amine group in amino acids with acids.

Specification Reference 6.2.2

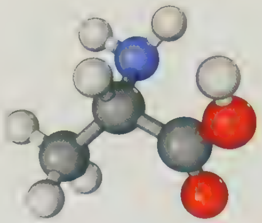


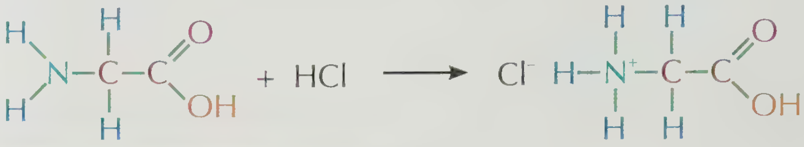
Figure 2: *Model of the amino acid alanine which has CH_3 as the R group.*

Tip: Amino acids are really important for life — they join together to form proteins in our bodies.

Tip: A conjugate base is just the deprotonated form of an acid. A conjugate acid is the protonated form of a base.

Example

Aminoethanoic acid will react with hydrochloric acid to form the salt of its conjugate acid:



Formation of esters

Just like other carboxylic acids, the carboxylic acid group in an amino acid can react with an alcohol in the presence of a strong acid catalyst (normally sulfuric acid) to form an ester.

Tip: See page 458 for more on the reactions of carboxylic acids.

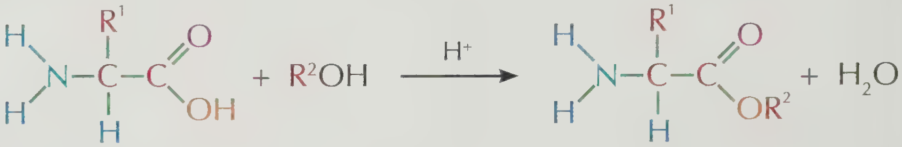
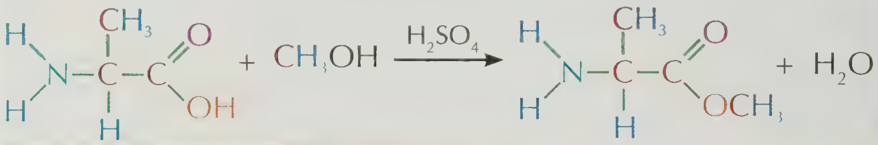


Figure 5: The reaction of an amino acid with an alcohol in acid to form an ester.

Tip: Just like in the esterification of carboxylic acids, the whole of the -OR group in the new ester product comes from the alcohol.

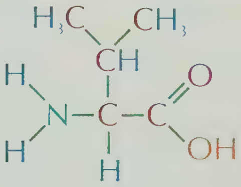
Example

2-aminopropanoic acid will react with methanol in the presence of sulfuric acid to form methyl-2-aminopropanoate.



Practice Question — Application

Q1 The amino acid valine is shown below:



a) Write an equation for the reaction between valine and sodium hydroxide.

b) Write an equation for the reaction between valine and hydrogen bromide

c) Write an equation for the reaction between valine and 2-methylpropan-1-ol in the presence of sulfuric acid.

Practice Questions — Fact Recall

Q1 What is the general formula of an α-amino acid?

Q2 What two key functional groups are found in amino acids?

Q3 Draw the general structure of an α-amino acid, using R to represent the variable group.

3. Chirality

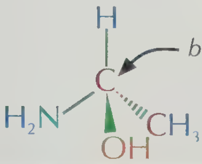
When a carbon atom is attached to four different groups, the groups can be arranged in two different ways around the carbon atom. This leads to two stereoisomers, called optical isomers, being formed.

Optical isomerism

Stereoisomerism is when two molecules have the same structural formula, but a different arrangement of atoms in space. *E/Z* isomerism, which you met in Module 4 is one example of stereoisomerism, where atoms are arranged differently around a C=C double bond. **Optical isomerism** is another type of stereoisomerism. Optical isomers have a **chiral** carbon atom. A chiral (or asymmetric) carbon atom is one that has four different groups attached to it.

Example

The molecule below, 1-aminoethanol, has a chiral carbon atom.

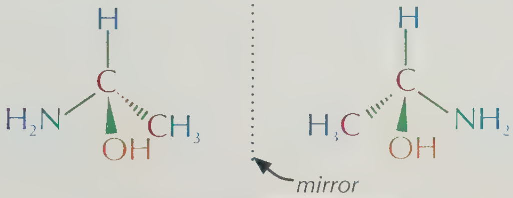


This carbon is chiral because it has four different groups attached to it.

It's possible to arrange the groups in two different ways around chiral carbon atoms so that two different molecules are made — these molecules are called **enantiomers** or optical isomers. The enantiomers are mirror images and no matter which way you turn them, they can't be superimposed.

Example — **Maths Skills**

Here are the two enantiomers of 1-aminoethanol. It doesn't matter how many times you turn and twist them, they can't be superimposed.



One enantiomer is usually labelled D and the other L — luckily you don't have to worry about which is which. Chiral compounds are very common in nature, but you usually only find one of the enantiomers — for example, all naturally occurring amino acids are L-amino acids (except glycine which isn't chiral) and most sugars are D-isomers.

Optical isomers are optically active — they rotate plane-polarised light. The two enantiomers of an optically active molecule will rotate the plane-polarised light in opposite directions. One enantiomer rotates it in a clockwise direction, and the other rotates it in an anticlockwise direction.

Drawing optical isomers

You have to be able to draw optical isomers. Just follow these steps each time:

1. Locate the chiral centre — look for the carbon atom with four different groups attached.
2. Draw one enantiomer in a tetrahedral shape — put the chiral carbon atom at the centre and the four different groups in a tetrahedral shape around it. Don't try to draw the full structure of each group — it gets confusing.

Learning Objectives:

- Know that optical isomerism is an example of stereoisomerism.
- Be able to describe optical isomers as non-superimposable mirror images about a chiral centre.
- Be able to identify chiral centres in a molecule of any organic compound.

Specification Reference 6.2.2

Tip: The best way to get your head around optical isomerism is to get a molecular modelling kit and have a go at making the isomers yourself. Give it a go — you know you want to.

Tip: If molecules can be superimposed, they're achiral — and there's no optical isomerism.

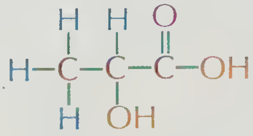
Figure 1: *Left-handed and right-handed scissors. These pairs of scissors are mirror images of each other — look closely and you'll see that they can't be superimposed on each other.*

3. Draw the mirror image of the enantiomer — put in a mirror line next to the enantiomer and then draw the mirror image of the enantiomer on the other side of it.

Don't panic. There are some examples below to help you get to grips with this.

Example — Maths Skills

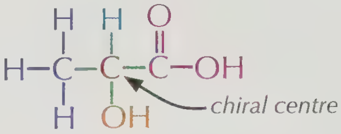
Draw the two enantiomers of 2-hydroxypropanoic acid.
The structure of 2-hydroxypropanoic acid is shown below.



$$\begin{array}{ccccccc} & & H & & H & & O \\ & & | & & | & & \| \\ H & - & C & - & C & - & C-OH \\ & & | & & | & & \\ & & H & & OH & & \end{array}$$

Tip: The chiral centre and the chiral carbon atom are the same thing.

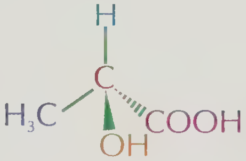
1. Locate the chiral centre — the chiral carbon in this molecule is the carbon with the groups H, OH, COOH and CH_3 attached.



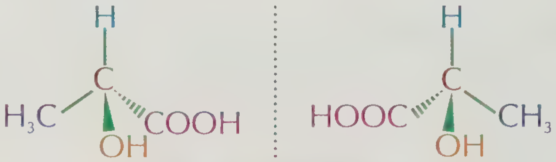
$$\begin{array}{ccccccc} & & H & & H & & O \\ & & | & & | & & \| \\ H & - & C & - & C & - & C-OH \\ & & | & & | & & \\ & & H & & OH & & \end{array}$$

Tip: Remember, those dashed lines mean the bond is pointing into the page and the solid wedged lines mean the bond is pointing out of the page towards you.

2. Draw one enantiomer in a tetrahedral shape — put the chiral carbon atom at the centre and the groups H, OH, COOH and CH_3 in a tetrahedral shape around it.



3. Then draw its mirror image beside it.



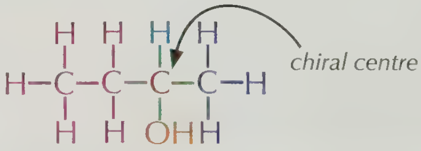
If you're just given the structural formula of a molecule in the exam, the easiest way to spot any chiral centres is to draw out the displayed formula first.

Tip: Don't forget, the chiral carbon is the one with four different groups attached to it.

Example — Maths Skills

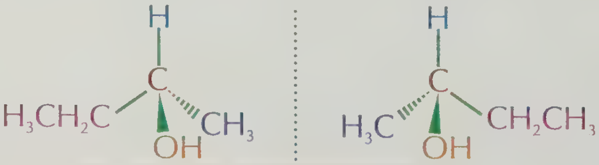
Draw the two enantiomers of butan-2-ol ($CH_3CH_2CHOHCH_3$).

Draw out the displayed formula and locate the chiral centre.



$$\begin{array}{ccccccccc} & & H & & H & & H & & H \\ & & | & & | & & | & & | \\ H & - & C & - & C & - & C & - & C-H \\ & & | & & | & & | & & | \\ & & H & & H & & OH & & H \end{array}$$

Draw one enantiomer in a tetrahedral shape, then draw its mirror image beside it.

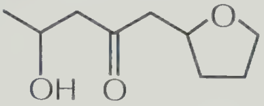


Molecules with more than one chiral carbon

Some molecules contain more than one chiral carbon, and you need to be able to spot them all.

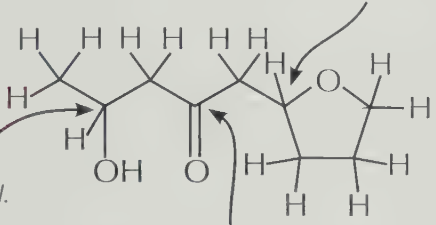
Example — **Maths Skills**

Circle all the chiral centres in the following organic molecule:



The structure shown is a skeletal formula — to find the carbon atoms that have four different groups attached, it can be helpful to show all the hydrogen atoms as well.

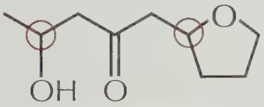
Although this carbon is attached to the same ring twice, it's chiral because the order of the atoms in the ring is different depending on which way round you go. Going clockwise round the ring from the chiral carbon you get -O-CH_2-CH_2-CH_2-, whilst going anticlockwise you get -CH_2-CH_2-CH_2-O-. So they count as two different groups.



This carbon has four different groups attached, so it's chiral.

A carbon needs to have four different groups attached to be chiral, so this carbon is achiral, even though the three groups it's attached to are different.

The chiral centres are:

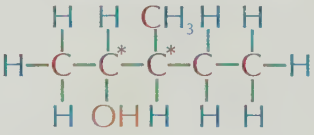


Tip: In skeletal formulas, the carbon atoms are located on the corners of the chain, and at the ends of bonds that don't have any other atoms attached. The C–H hydrogen atoms aren't shown at all.

If a molecule has more than one chiral centre, it will have more than two optical isomers.

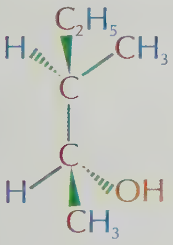
Example — **Maths Skills**

The molecule on the right is 3-methylpentan-2-ol. It contains two chiral carbons, marked with asterisks.

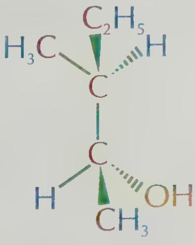


$$H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{OH}{C^*}}-\overset{CH_3}{\underset{H}{C^*}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H$$

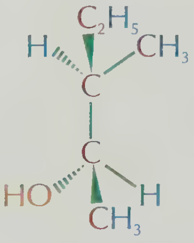
As a result, there are four different optical isomers of this molecule:



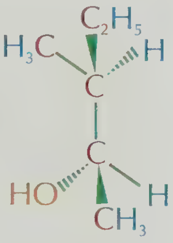
Initial drawing of molecule.



Just top carbon mirror imaged.



Just bottom carbon mirror imaged.



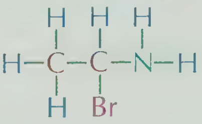
Both carbons mirror imaged.

Tip: To make sure you get all the enantiomers of a molecule with more than one chiral carbon, first draw out the molecule with both chiral centres shown in 3D. Then draw it again, with the mirror image of one of the chiral carbons. Then draw it with the mirror image of the other chiral carbon. Then draw it with both chiral carbons mirror imaged. If you do this every time, you'll get all the enantiomers and won't accidentally draw one twice.

Practice Questions — Application

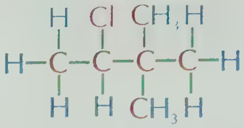
Q1 Circle the chiral carbon(s) in each of these molecules.

a)



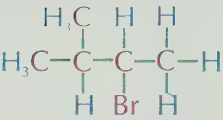
$$\begin{array}{ccccccccc} & & H & & H & & H & & \\ & & | & & | & & | & & \\ H & - & C & - & C & - & N & - & H \\ & & | & & | & & & & \\ & & H & & Br & & & & \end{array}$$

b)



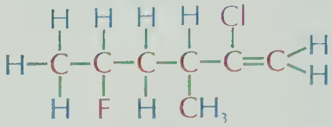
$$\begin{array}{ccccccccccc} & & H & & Cl & & CH_3 & & H & & \\ & & | & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & | & & \\ & & H & & H & & CH_3 & & H & & \end{array}$$

c)



$$\begin{array}{ccccccccc} & & H_3C & & H & & H & & \\ & & | & & | & & | & & \\ H_3C & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & \\ & & H & & Br & & H & & \end{array}$$

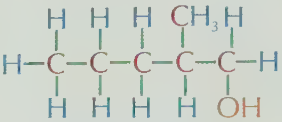
d)



$$\begin{array}{ccccccccccccc} & & H & & H & & H & & H & & Cl & & \\ & & | & & | & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & C & - & C & = & C\begin{smallmatrix}\diagup H \\ \diagdown H\end{smallmatrix} \\ & & | & & | & & | & & | & & & & \\ & & H & & F & & H & & CH_3 & & & & \end{array}$$

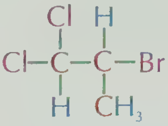
Q2 Draw the two enantiomers of the following molecules.

a)



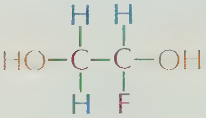
$$\begin{array}{ccccccccccccc} & & H & & H & & H & & CH_3 & & H & & \\ & & | & & | & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & | & & | & & \\ & & H & & H & & H & & H & & OH & & \end{array}$$

b)



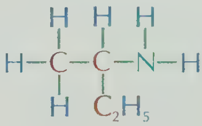
$$\begin{array}{ccccccc} & & Cl & & H & & \\ & & | & & | & & \\ Cl & - & C & - & C & - & Br \\ & & | & & | & & \\ & & H & & CH_3 & & \end{array}$$

c)



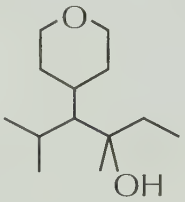
$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ HO & - & C & - & C & - & OH \\ & & | & & | & & \\ & & H & & F & & \end{array}$$

d)

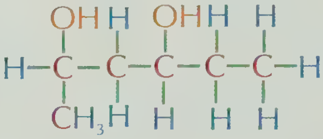


$$\begin{array}{ccccccccc} & & H & & H & & H & & \\ & & | & & | & & | & & \\ H & - & C & - & C & - & N & - & H \\ & & | & & | & & & & \\ & & H & & C_2H_5 & & & & \end{array}$$

Q3 Circle all the chiral centres in the following molecule:

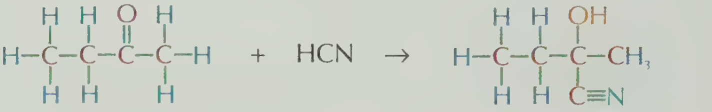


Q4 Draw all the enantiomers of the following molecule:



$$\begin{array}{ccccccccccccc} & & OH & & H & & OH & & H & & H & & \\ & & | & & | & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & | & & | & & \\ & & CH_3 & & H & & H & & H & & H & & \end{array}$$

Q5 Here is an equation for the reaction between butanone and HCN.



$$\begin{array}{ccccccccc} & & H & & H & & O & & H \\ & & | & & | & & \| & & | \\ H & - & C & - & C & - & C & - & C & - & H \\ & & | & & | & & & & | \\ & & H & & H & & & & H \end{array} \quad + \quad HCN \quad \rightarrow \quad \begin{array}{ccccccc} & & H & & H & & OH \\ & & | & & | & & | \\ H & - & C & - & C & - & C & - & CH_3 \\ & & | & & | & & | \\ & & H & & H & & C{\equiv}N \end{array}$$

butanone *2-hydroxy-2-methylbutanenitrile*

Draw the two optical isomers that can be formed via this reaction.

Tip: When you're drawing out the enantiomers for molecules just write out the structural formula of each group — don't try and draw the displayed formula for each one or your diagram will become too confusing.

Practice Questions — Fact Recall

Q1 What is a stereoisomer?

Q2 What is optical isomerism?

Q3 What is a chiral carbon?

4. Addition Polymers

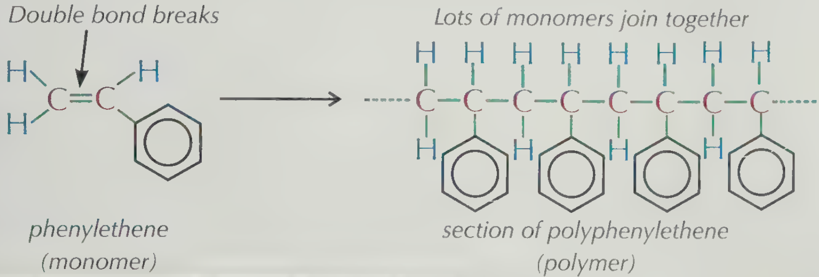
Lots of small molecules (called monomers) can join together to form really long molecules (called polymers). Polymers that are formed from alkenes are called addition polymers. You met these on pages 236-239 but here's a recap...

What are addition polymers?

The double bonds in alkenes or substituted alkenes can break and then join together to make long chains called **addition polymers**. It's like they're holding hands in a big line. The individual, small molecules are called **monomers** and the process of making an addition polymer is called addition polymerisation.

Example

Polyphenylethene is made by the addition polymerisation of phenylethene:

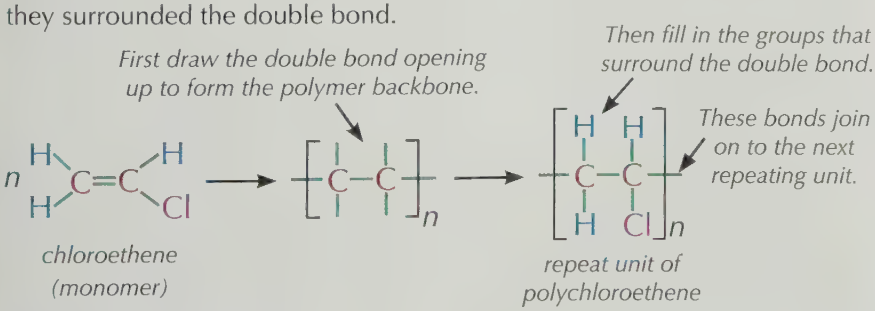

Double bond breaks
Lots of monomers join together
phenylethene
(monomer)
section of polyphenylethene
(polymer)

Repeat units

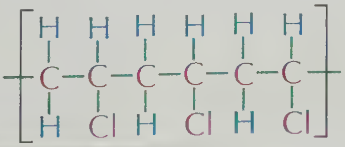
Addition polymers are made up of **repeat units** (a bit of molecule that repeats over and over again). The repeat unit looks very similar to the monomer but the double bond has opened out. You can spot that a polymer is an addition polymer because the main chain of the repeat unit will only contain carbon-carbon bonds. You need to be able to draw repeat units from the structure of a monomer and vice versa.

Example

Polychloroethene is made from chloroethene. To draw the repeating unit of polychloroethene, first draw the two C=C carbons, replace the double bond with a single bond and add a bond to each of the carbons. This forms the polymer backbone. Then just fill in the rest of the groups in the same way they surrounded the double bond.


First draw the double bond opening up to form the polymer backbone.
Then fill in the groups that surround the double bond.
These bonds join on to the next repeating unit.
chloroethene
(monomer)
repeat unit of
polychloroethene

The polymer chain is made up of repeat units joined together, so this is what a section of the chain would look like:



Learning Objectives:

- Be able to predict whether a polymer has formed by addition polymerisation.
- Be able to predict the repeat unit of an addition polymer from a given monomer.
- Be able to predict the monomer required for a given section of an addition polymer molecule.

Specification Reference 6.2.3

Tip: Polyphenylethene is more commonly known as polystyrene.

Figure 1: *Two different forms of polyphenylethene. Expanded polyphenylethene is used in packaging and high density polyphenylethene is used to make plastic models.*

Tip: The '*n*' after the brackets is the number of repeat units in the polymer.

Exam Tip

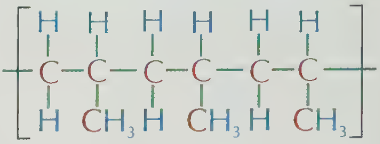
Make sure you draw the bonds that join onto the next repeat unit, or you may lose marks in the exam.

Finding the monomer of a polymer chain

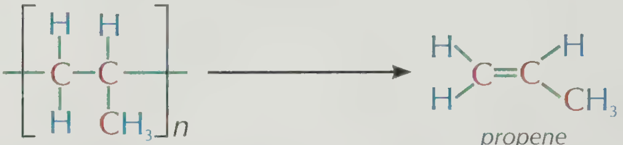
To draw the monomer from a polymer chain, you first need to find the repeat unit. For an addition polymer, the backbone of the repeat unit will always be two carbons long. Then, to find the monomer, you need to remove the empty bonds (which join on to the next repeat unit) and replace the central carbon-carbon bond with a double bond.

Example

A section of the polymer chain of polypropene is shown on the right:



The main chain of the polymer only contains carbon atoms, so it's an addition polymer. This means the repeat unit will contain a two-carbon section from the main polymer chain:



repeat unit of polypropene

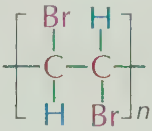
propene (monomer)

Tip: The names of polymers can be written with or without the brackets — e.g. poly(propene) or polypropene.

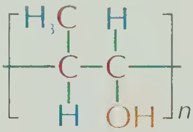
Practice Questions — Application

Q1 Draw the monomers that formed these repeat units:

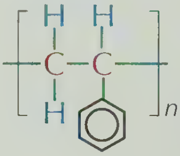
a)



b)

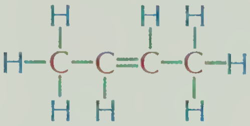


c)

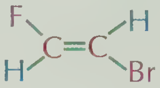


Q2 Draw the repeat units of the polymers that would be formed from these monomers:

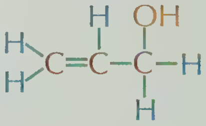
a)



b)

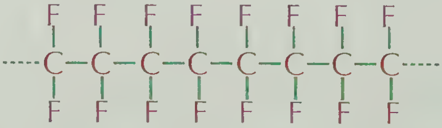


c)



Tip: There isn't too much to learn about addition polymers but you're going to need to know about condensation polymers too — they're covered in the next topic.

Q3 Teflon® is a polymer commonly used to coat non-stick pans. The structure of a short stretch of Teflon® is shown below.



Draw the structure of the monomer that's used to make Teflon®.

***Figure 2:** A Teflon® coated frying pan.*

Practice Questions — Fact Recall

Q1 What types of monomers form addition polymers?

Q2 What name is given to the process of forming an addition polymer?

Q3 What is a repeat unit?

5. Condensation Polymers

Addition polymers aren't the only type of polymers you need to know about. You also need to know about condensation polymers — they're a bit different. Read on to find out more...

What are condensation polymers?

Condensation polymerisation usually involves two different types of monomer. Each monomer has at least two functional groups. The functional groups react to form a link, creating polymer chains. Each time a link is formed, a small molecule is lost (often water) — that's why it's called condensation polymerisation.

Examples of **condensation polymers** include polyamides and polyesters. In polyesters, an ester link (–COO–) is formed between the monomers. In polyamides, amide links (–CONH–) are formed between the monomers.

Polyamides

Reactions between dicarboxylic acids and diamines make **polyamides**. The carboxyl groups of dicarboxylic acids react with the amino groups of diamines to form **amide links**. A water molecule is lost each time an amide link is formed — it's a condensation reaction (see Figure 1).

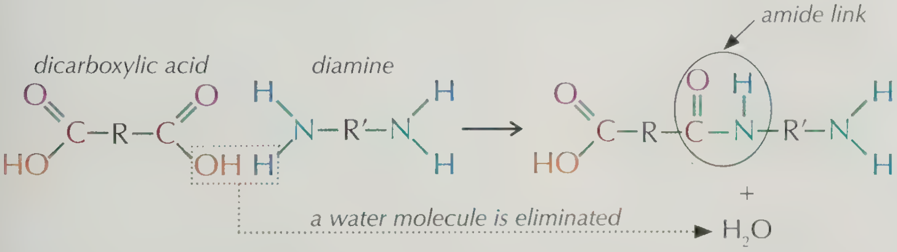
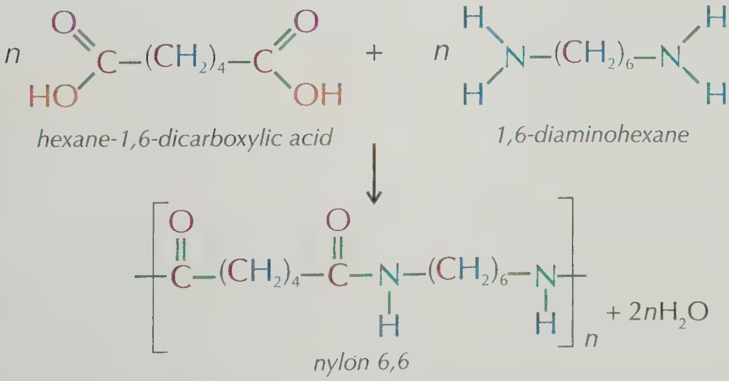


Figure 1: *The formation of an amide link.*

Dicarboxylic acids and diamines have functional groups at both ends, which means that they can each form two amide links and long chains can form.

Examples

Nylon 6,6 is made from hexane-1,6-dicarboxylic acid and 1,6-diaminohexane:



Nylon fibre is very strong, elastic and quite abrasion-resistant (it won't wear away easily).

Learning Objectives:

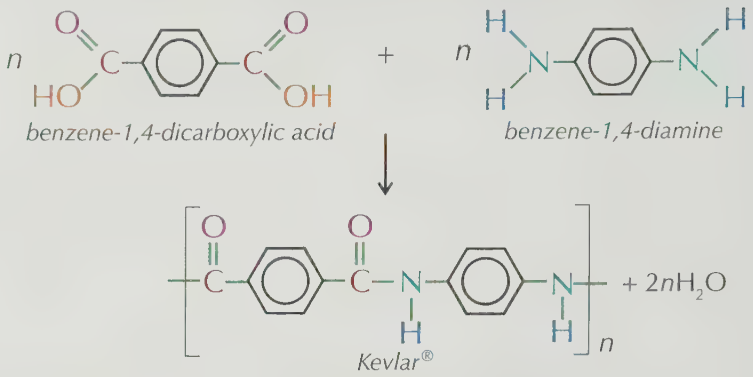
- Be able to describe how polyesters are formed by condensation polymerisation.
- Be able to describe how polyamides are formed by condensation polymerisation.
- Be able to describe the acid and base hydrolysis of the ester groups in polyesters and the amide groups in polyamides.
- Be able to predict the repeat unit of a condensation polymer from a given monomer(s).
- Be able to predict the monomer(s) required for a given section of a condensation polymer molecule.
- Be able to predict whether a given polymer has formed by condensation polymerisation.

Specification Reference 6.2.3

Tip: The formation of polyamides is very similar to the formation of polyesters (next page).

Figure 2: *A bulletproof vest made out of Kevlar®.*

Kevlar® is made from benzene-1,4-dicarboxylic acid and benzene-1,4-diamine:


n
benzene-1,4-dicarboxylic acid
+
n
benzene-1,4-diamine
+ 2nH₂O
n
Kevlar®

Kevlar® is really strong and light — five times stronger than steel. It's not stretchy, and is quite stiff. It's most famous for its use in bulletproof vests.

Polyesters

The carboxyl groups of dicarboxylic acids can react with the hydroxyl groups of diols to form **ester links** — it's another condensation reaction (see Figure 3).

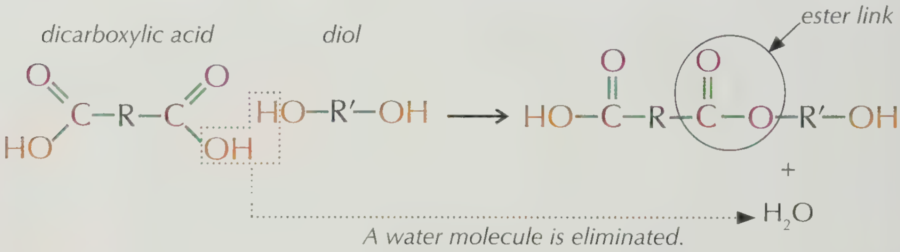

dicarboxylic acid
diol
ester link
+
H₂O
A water molecule is eliminated.

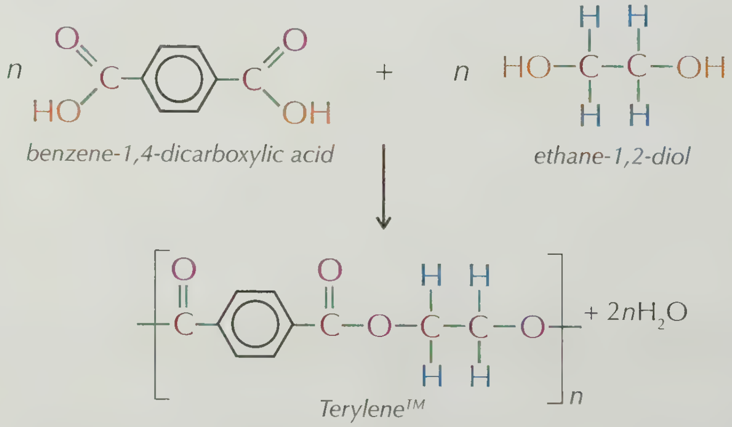
Figure 3: *The formation of an ester link.*

Figure 4: *Scanning electron microscopy of synthetic polyester fibres.*

Polymers that are joined by ester links are called **polyesters**. Polyester fibres are used in clothing — they are strong (but not as strong as nylon), flexible and abrasion-resistant.

Examples

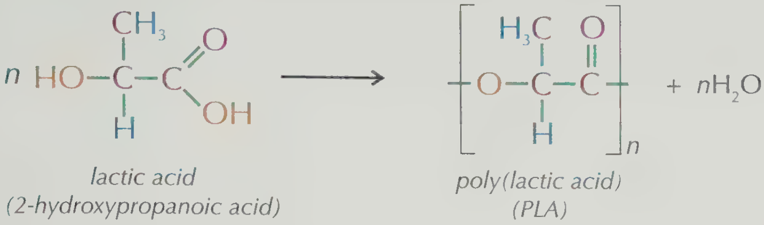
Terylene™ (PET) is formed from benzene-1,4-dicarboxylic acid and ethane-1,2-diol.


n
benzene-1,4-dicarboxylic acid
+
n
ethane-1,2-diol
+ 2nH₂O
n
Terylene™

Terylene™ is used in clothes to keep them crease-free and make them last longer.

Figure 5: *The containers that microwave meals come in are made of Terylene™.*

Poly(lactic acid) (PLA) is made from lactic acid (2-hydroxypropanoic acid). Lactic acid monomers can form polymers on their own because they contain both a hydroxy group and a carboxylic acid group.


n
lactic acid
(2-hydroxypropanoic acid)
+ nH₂O
n
poly(lactic acid)
(PLA)

Poly(lactic acid) is a biodegradable and renewable polymer.

Figure 6: *A cup made out of poly(lactic acid) or PLA. This cup is made from renewable materials and is biodegradable.*

Hydrolysis of polyesters and polyamides

The ester or amide link in polyesters and polyamides can be broken down by **hydrolysis** — water molecules are added back in and the links are broken. The products of the hydrolysis are the monomers that were used to make the polymer — you're basically reversing the condensation reaction that was used to make them:

$$n(\text{monomers}) \underset{\text{hydrolysis}}{\overset{\text{condensation}}{\rightleftharpoons}} \text{polymer} + \text{water}$$

In practice, hydrolysis with just water is far too slow, so the reaction is done with an acid or a base. Polyamides will hydrolyse more easily with an acid than a base. The general equation for the acid hydrolysis of a polyamide is shown below:

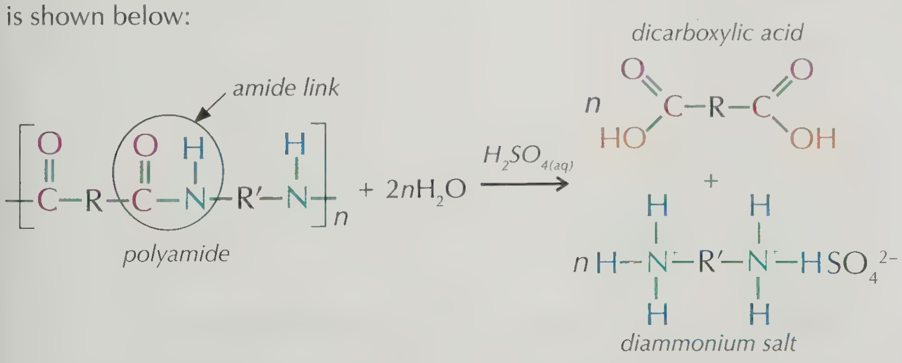

amide link
polyamide
+ 2nH₂O
H₂SO₄(aq)
dicarboxylic acid
n
+
n
diammonium salt

Figure 7: *The acid catalysed hydrolysis of a polyamide.*

Tip: If you were to acid hydrolyse a polyester you would get a diol instead of a diamine, but other than that the equation would be exactly the same.

Polyesters will hydrolyse more easily with a base. A metal salt of the dicarboxylic acid is formed.

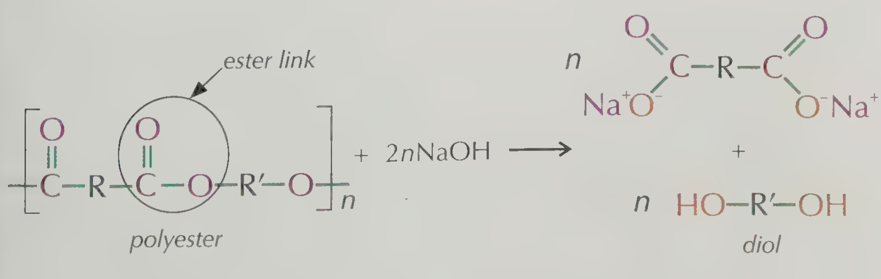

ester link
polyester
+ 2nNaOH
dicarboxylic acid salt
n
+
n HO–R′–OH
diol

Figure 8: *The base catalysed hydrolysis of a polyester.*

Tip: If you were to hydrolyse a polyamide with a base you would get a diamine instead of a diol.

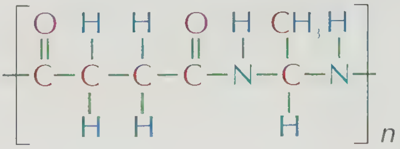
Identifying monomers

In your exam, you might be asked to identify the monomers that formed a particular condensation polymer. To do this just follow these steps:

- Remove the bond in the middle of the amide or ester links — that's the bond between the C=O group and the NH group in polyamides or the bond between the C=O group and the oxygen in polyesters.
- Add OH groups on to the C=O groups to make carboxyl groups.
- For polyamides, add hydrogens on to the NH groups to make NH_2 groups.
- For polyesters, add hydrogens on to the oxygens to make OH groups and add OH groups on to any terminal carbon atoms.

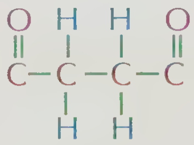
Example

Draw the monomers that formed this condensation polymer:

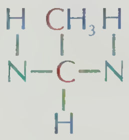


Tip: This example is a polyamide. You do exactly the same for a polyester but you end up with a dicarboxylic acid and a diol.

This is a polyamide so if you remove the bond in the middle of the amide link you get:



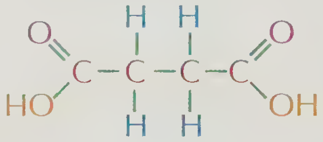
and

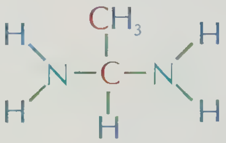


Exam Tip
Don't be caught out — there won't necessarily be two different monomers. There could be one monomer with a COOH and an NH_2 group on it.

Adding an OH group on to the C=O groups gives you:

And adding a hydrogen on to each of the NH groups gives you:





So these must be the monomers that joined to form the polymer.

Finding repeat units from monomers

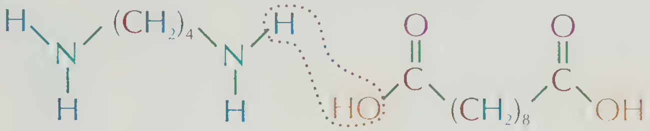
If you know the formulas of a pair of monomers that react together in a condensation polymerisation reaction, you can work out the repeat unit of the condensation polymer that they would form. Here are the steps you should take:

- Draw out the two monomer molecules next to each other.
- Remove an OH from the dicarboxylic acid, and an H from the nitrogen atom in the diamine — that gives you a water molecule.
- Join the C and the N together to make an amide link.
- Take another H and OH off the ends of your molecule.
- Draw brackets around your structure, with the bonds at the ends of the structure extending through the brackets. There's your repeat unit.

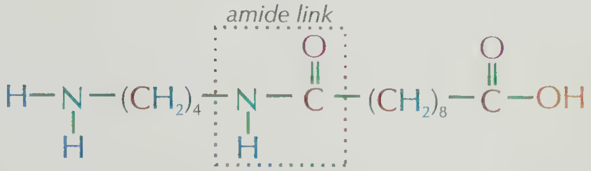
Example

Draw the repeat unit of the condensation polymer that is made from 1,4-diaminobutane, $H_2N(CH_2)_4NH_2$, and decanedioic acid, $HOOC(CH_2)_8COOH$.

If you draw out the monomers next to each other, this makes it easier to see which groups will be lost to form the water molecule:

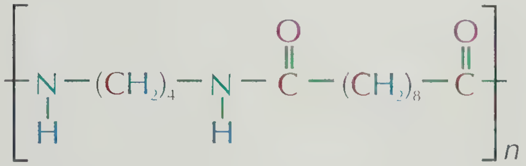


Draw a bond between the C and the N that have lost groups to the water molecule:



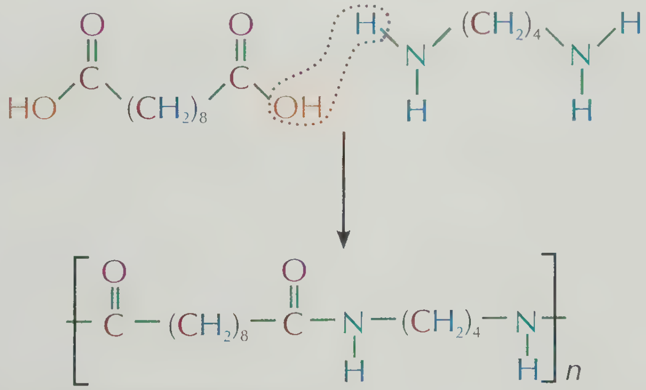
$$H-\underset{H}{N}-(CH_2)_4-\underset{H}{N}-\overset{O}{\overset{\|}{C}}-(CH_2)_8-\overset{O}{\overset{\|}{C}}-OH$$

To get the repeat unit, all that needs to be done now is to remove another -OH and -H from the groups at the ends of the molecule and add brackets. Add an '*n*' after the brackets, too.



$$\left[-\underset{H}{N}-(CH_2)_4-\underset{H}{N}-\overset{O}{\overset{\|}{C}}-(CH_2)_8-\overset{O}{\overset{\|}{C}}-\right]_n$$

If you start by drawing the monomers the other way round, your repeat unit may end up looking slightly different:



More complex condensation polymers

Not all condensation polymers are made up from a dicarboxylic acid and a diamine or diol. For example, molecules that contain both an amine and an alcohol group can react with dicarboxylic acids in a condensation polymerisation reaction. The polymers they form contain both amide and ester links.

Tip: Even if you've got a dicarboxylic acid and a diol, the -OH group is always lost from the carboxylic acid.

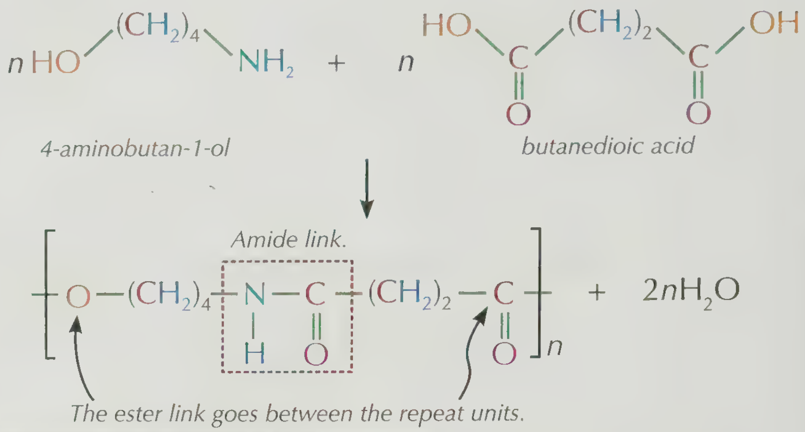
Tip: You could have a monomer that contains an acyl chloride group rather than a carboxylic acid group. To draw the polymer, the steps are exactly the same except rather than removing an -OH group from the C=O carbon, you'll remove a chlorine atom. This means a molecule of HCl (rather than water) is lost.

Tip: If you've got a diol rather than a diamine, the process is exactly the same except you end up with a polyester rather than a polyamide.

Tip: It doesn't matter which way round you draw the repeat unit — both ways are correct.

Example

4-aminobutan-1-ol contains an amine and an alcohol group. It can react with dicarboxylic acids, such as butanedioic acid, in a condensation polymerisation reaction:

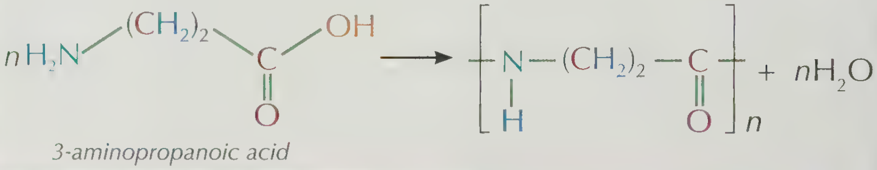


Tip: You could also draw the repeat unit so that the ester link is in the middle and the amide link is split between the repeat units — both ways are correct.

If a molecule contains a carboxylic acid group and either an alcohol or an amine group, it can polymerise with itself to from a condensation polymer with only one monomer.

Example

3-aminopropanoic acid contains both an amine and a carboxylic acid group. It can react with itself to form a condensation polymer:

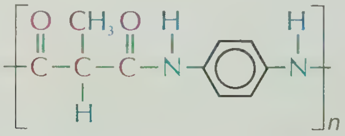


Tip: When a molecule can form a condensation polymer with itself, it's called 'self polymerisation'.

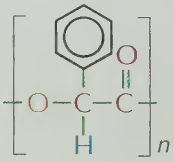
Practice Questions — Application

Q1 Identify whether the following are formulas of polyesters or polyamides and draw the monomer(s) they were formed from.

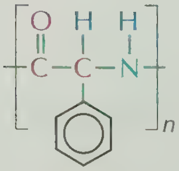
a)



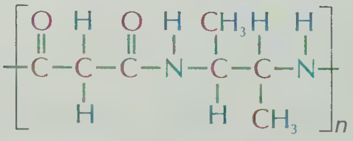
b)



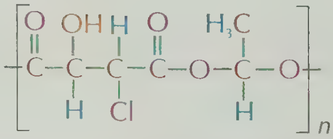
c)



d)



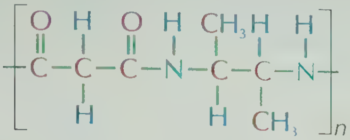
e)



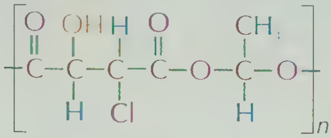
Tip: If you think that a polymer was made from only one monomer, you'll need to look at both ends of the repeating unit to work out what type of polymer (polyester or polyamide) it is.

Q2 Write equations for the acid hydrolysis of the following polymers:

a)

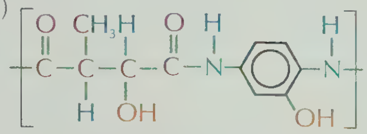


b)

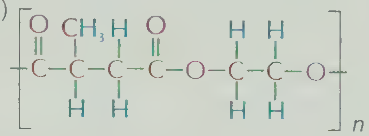


Q3 Write equations for the hydrolysis of the following polymers in the presence of NaOH.

a)

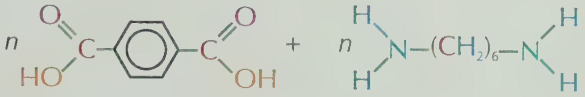


b)

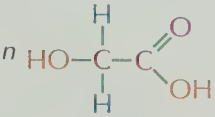


Q4 Draw the repeat units of the polymers that would be formed from these monomers:

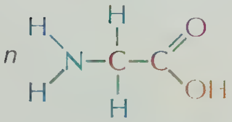
a)



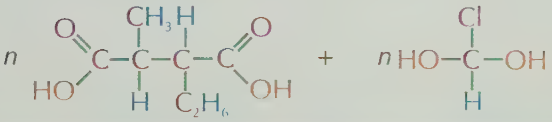
b)



c)



d)



Exam Tip
In the exam, you could also be asked to compare condensation polymers with addition polymers (which were covered on pages 479-480). So you need to know the details of both types of polymerisation.

Practice Questions — Fact Recall

Q1 What small molecule is released when a condensation polymer forms from a dicarboxylic acid and a diamine?

Q2 Name the types of molecules that can join together to form:

a) polyamides b) polyesters

Q3 Name the type of link that joins the monomers together in:

a) polyamides b) polyesters

Q4 Why is hydrolysis performed in the presence of an acid or a base, as opposed to just using water?

Q5 What are the products when polyesters are hydrolysed in the presence of an alkali?

Section Summary

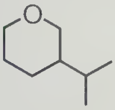
Make sure you know...

- What amines are and how to name them.
- That amines are bases and can donate their lone pair of electrons to a proton to form a dative (coordinate) bond.
- The reactions of amines with acids to form ammonium salts.
- That you can make aliphatic amines from haloalkanes and excess ethanolic ammonia.
- How to make aromatic amines by reducing aromatic nitro compounds with tin and hydrochloric acid.
- What amides are and how to name them.
- The difference between primary and secondary amides.
- That amino acids are molecules that contain an amino group and a carboxylic acid group.
- That α-amino acids have the amino and carboxylic acid groups on the same carbon.
- That the general formula of an α-amino acid is $RCH(NH_2)COOH$.
- That the carboxylic acid group in amino acids can react with alkalis to form a salt.
- That the amine group in amino acids can react with acids to form a salt.
- That the carboxylic acid group in amino acids can react with alcohols in the presence of an acid catalyst to form esters.
- That optical isomerism is a type of stereoisomerism.
- That optical isomers are non-superimposable mirror images.
- That chiral molecules can form optical isomers.
- How to identify chiral centres.
- How to draw optical isomers.
- That addition polymers are formed through the polymerisation of alkenes and substituted alkenes.
- How to predict the repeat unit of an addition polymer from a monomer.
- How to identify the monomer that makes up a section of an addition polymer chain.
- That condensation polymerisation forms polymers through the loss of a small molecule.
- That condensation polymers are held together by ester or amide linkages.
- That polyamides are formed through the condensation polymerisation of dicarboxylic acids and diamines.
- That polyesters are formed through condensation polymerisation when carboxylic acid and alcohol functional groups react.
- That condensation polymers can be broken down by hydrolysis.
- How polyesters and polyamides can be hydrolysed in the presence of acids and bases.
- How to predict the repeat unit of a condensation polymer from (a) given monomer(s).
- How to identify the monomer(s) that a given condensation polymer was formed from.
- How to identify whether addition or condensation polymerisation will/has taken place from given monomers or a section of polymer.

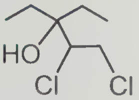
Exam-style Questions

1 Which of the following molecules contains two chiral carbons?

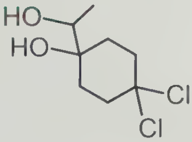
A



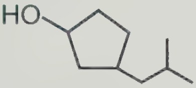
B



C

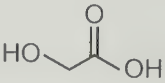


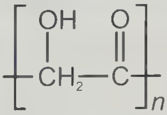
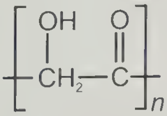
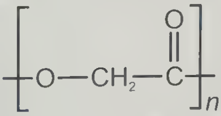
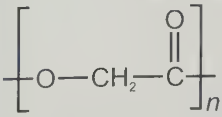
D



(1 mark)

2 Which of the options below shows the correct repeat unit and type of polymerisation that occurs when the following molecule is polymerised?



	Repeat Unit	**Type of Polymerisation**
A	 $\left[-\overset{\text{OH}}{\overset{\vert}{\text{C}}}\text{H}_2-\overset{\text{O}}{\overset{\Vert}{\text{C}}}- \right]_n$	Condensation
B	 $\left[-\overset{\text{OH}}{\overset{\vert}{\text{C}}}\text{H}_2-\overset{\text{O}}{\overset{\Vert}{\text{C}}}- \right]_n$	Addition
C	 $\left[-\text{O}-\text{CH}_2-\overset{\text{O}}{\overset{\Vert}{\text{C}}}- \right]_n$	Condensation
D	 $\left[-\text{O}-\text{CH}_2-\overset{\text{O}}{\overset{\Vert}{\text{C}}}- \right]_n$	Addition

(1 mark)

3 Which of the following molecules would you not expect to find in the product mixture when 2-chlorobutane is reacted with an excess of ethanolic ammonia?

A $NH_4^+Cl^-$

B $CH_3CH_2CH_2CH_2NH_2$

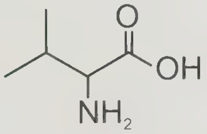
C $N(CH(CH_3)CH_2CH_3)_4^+$

D $NH(CH(CH_3)CH_2CH_3)_2$

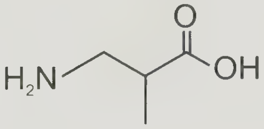
(1 mark)

4 This question is about amino acids and their properties.
The structures of three different amino acids are shown below:

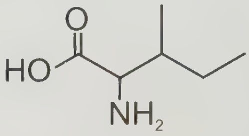
A



B



C



(a) (i) Which of the amino acids (**A**, **B** and **C**) are α-amino acids? Explain your answer.

(2 marks)

(ii) Write down the general formula of an α-amino acid.

(1 mark)

(b) The common name for amino acid **A** is valine.
Like many other amino acids, valine shows optical isomerism.

(i) Draw the two optical isomers of valine.

(2 marks)

(ii) Draw the skeletal structure of the molecule that would be formed if valine was heated under reflux with ethanol in the presence of an acid catalyst.

(1 mark)

(c) Amino acids can be involved in polymerisation reactions.

(i) Predict the type of polymerisation that amino acids will undergo.

(1 mark)

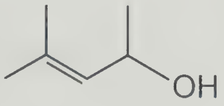
(ii) Draw a section of the polymer chain that would be formed from two molecules of amino acid **C**.

(1 mark)

(iii) Give the reagents and conditions needed to break down the polymer chain formed by amino acid **C** into its constituent monomers.

(1 mark)

5 A research chemist is investigating the reactions of 2-methyl-2-penten-4-ol, the structure of which is shown below:



2-methyl-2-penten-4-ol

(a) 2-methyl-2-penten-4-ol exhibits stereoisomerism.

(i) Explain what is meant by the term stereoisomer and state the type of stereoisomerism shown by 2-methyl-2-penten-4-ol.

(2 marks)

(ii) What feature of 2-methyl-2-penten-4-ol enables it to show stereoisomerism?

(1 mark)

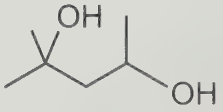
(iii) Draw two stereoisomers of 2-methyl-2-penten-4-ol.

(2 marks)

(b) Under certain conditions, 2-methyl-2-penten-4-ol will polymerise to form an addition polymer. Draw the repeat unit of the polymer formed when 2-methyl-2-penten-4-ol polymerises.

(1 mark)

(c) 2-methyl-2-penten-4-ol can be converted into 2-methylpentan-2,4-diol. The structure of 2-methylpentan-2,4-diol is shown below.

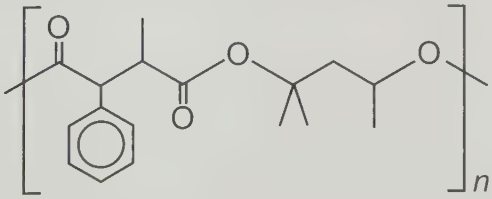


2-methylpentan-2,4-diol

Does 2-methylpentan-2,4-diol exhibit stereoisomerism? Explain your answer.

(2 marks)

(d) 2-methylpentan-2,4-diol can be used in a second synthesis reaction to form the condensation polymer shown below:



(i) Draw the structure of the molecule which would react with 2-methylpentan-2,4-diol to form this polymer.

(1 mark)

(ii) State what type of condensation polymer this is.

(1 mark)

1. Making Carbon-Carbon Bonds

Learning Objectives:

- Understand that C–C bond formation is used in synthesis to increase the length of a carbon chain
- Be able to describe the formation of C–C≡N by reaction of haloalkanes with CN^- and ethanol, including the nucleophilic substitution mechanism.
- Be able to describe the formation of C–C≡N by reaction of carbonyl compounds with HCN, including the nucleophilic addition mechanism.
- Be able to describe the reactions of nitriles by reduction (e.g. with H_2/Ni) to form amines and by acid hydrolysis to form carboxylic acids.
- Be able to describe the formation of a substituted aromatic C–C by alkylation (using a haloalkane) and acylation (using an acyl chloride) in the presence of a halogen carrier (Friedel-Crafts reaction).

Specification Reference 6.2.4

Organic Chemistry is all about carbon compounds and how they react. But getting one carbon to react with another and form a new carbon-carbon bond is surprisingly hard. Here are some reactions that let you do it.

Extending the carbon chain

In organic synthesis, it's useful to have ways of making a carbon chain longer. You can't just put two carbon chains together and expect them to react though. Instead, you have to use reactants and reagents that have a nucleophilic or electrophilic carbon atom.

Reactions of cyanide to form C–C bonds

Cyanide (CN^-) is an ion containing a negatively charged carbon atom, so it's a nucleophile (an electron pair donor). It'll react with carbon centres that have a slight positive charge to create a new carbon-carbon bond.

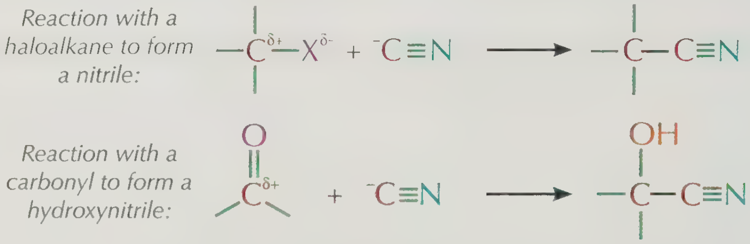

Reaction with a haloalkane to form a nitrile:
C
δ+
X
δ-
+
⁻C≡N
C
C≡N
Reaction with a carbonyl to form a hydroxynitrile:
O
C
δ+
+
⁻C≡N
OH
C
C≡N

Figure 1: *Reactions of cyanide ions with partially positive carbon centres to form new carbon-carbon bonds.*

So you can increase the length of a carbon chain by reacting an organic compound that contains a slightly positive carbon centre with a cyanide reagent such as potassium cyanide (KCN), sodium cyanide (NaCN) or hydrogen cyanide (HCN).

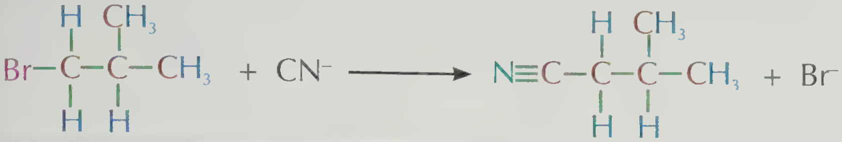
Reactions of cyanide with haloalkanes

Haloalkanes usually contain a polar carbon-halogen bond. The halogen is generally more electronegative than carbon, making the carbon electron deficient. You saw in Module 4 that nucleophiles, such as hydroxide ions and water, will react with the positive carbon centre in haloalkanes to replace the halogen atom. This is a nucleophilic substitution reaction. If you reflux a haloalkane with potassium (or sodium) cyanide in ethanol, then the cyanide ions can react with the haloalkane by nucleophilic substitution. This forms an organic compound that contains a -C≡N functional group where the halogen used to be — this is called a **nitrile**. The general equation for the reaction is:

$$R{-}X + CN^- \xrightarrow[\textit{reflux}]{\textit{ethanol}} R{-}C{\equiv}N + X^-$$

Example

When 1-bromo-2-methylpropane is heated under reflux with hydrogen cyanide in ethanol, it reacts to form 3-methylbutanenitrile:



$$Br-\overset{H}{\underset{H}{C}}-\overset{CH_3}{\underset{H}{C}}-CH_3 + CN^- \longrightarrow N\equiv C-\overset{H}{\underset{H}{C}}-\overset{CH_3}{\underset{H}{C}}-CH_3 + Br^-$$

Tip: You have to use ethanol as a solvent instead of water. If you used water, the water molecules could act as a competing nucleophile and you'd get some alcohol product.

This is the mechanism for the nucleophilic substitution reaction between cyanide and a haloalkane, using bromoethane as an example:

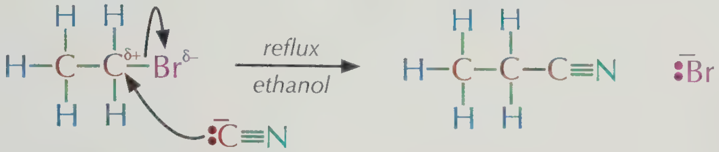


Figure 2: *The mechanism of the nucleophilic substitution reaction between a haloalkane and cyanide.*

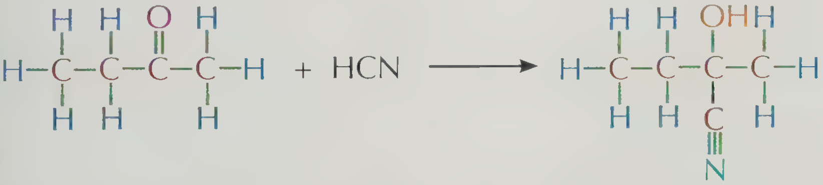
Reactions of cyanide with carbonyls

Aldehydes and ketones are both carbonyl compounds — they contain a polar C=O bond. If you mix them with hydrogen cyanide, the cyanide ion will react with the positive carbon centre to form -C(OH)C≡N group — this is called a **hydroxynitrile**.

Tip: There's more about the reactions of carbonyl compounds on pages 454-456.

Example

Butanone reacts with hydrogen cyanide in a nucleophilic addition reaction to form 2-hydroxy-2-methylbutanenitrile:



$$H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{O}{\overset{\|}{C}}-\overset{H}{\underset{H}{C}}-H + HCN \longrightarrow H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{OH}{\underset{C\equiv N}{C}}-\overset{H}{\underset{H}{C}}-H$$

butanone *2-hydroxy-2-methylbutanenitrile*

The reaction is an example of a nucleophilic addition reaction. The general mechanism for the reaction is:

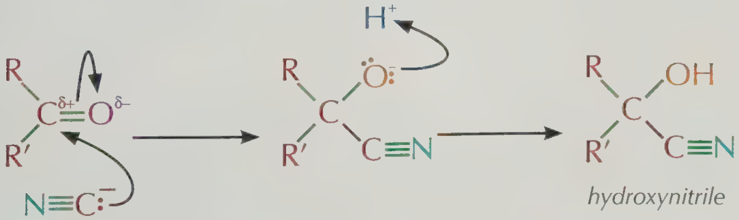


Figure 3: *The mechanism of the nucleophilic addition reaction between a carbonyl and cyanide.*

Tip: Hydrogen cyanide could also be called methane nitrile. Hydrogen cyanide is the molecule's old name and methane nitrile is its name assigned by the IUPAC naming conventions. Hydrogen cyanide is more common, so this is the name you should use.

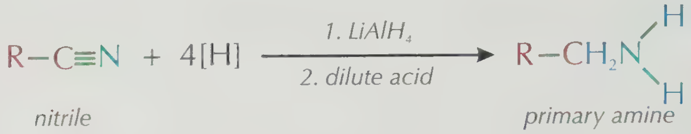
Reactions of nitrile groups

Once you've added another carbon atom onto the carbon chain and formed a nitrile (or a hydroxynitrile), it's easy to convert the nitrile into a new functional group. This is because nitrile groups are very reactive. This is really useful in synthesis — you can make a number of different compounds from a nitrile.

Reduction of nitriles

You can reduce a nitrile to a primary amine by a number of different methods.

1. You can use lithium aluminium hydride ($LiAlH_4$ — a strong reducing agent), followed by some dilute acid.
   The general equation for the reaction with a nitrile is:

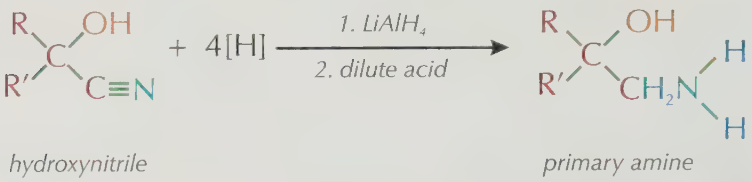


$$R{-}C{\equiv}N + 4[H] \xrightarrow[\text{2. dilute acid}]{\text{1. } LiAlH_4} R{-}CH_2NH_2$$

nitrile
primary amine

Figure 4: *The general reaction for the reduction of a nitrile with $LiAlH_4$.*

You can also reduce hydroxynitriles using this method.
The general equation for the reaction is:



R
OH
R′
C
C≡N
+ 4[H]
1. LiAlH₄
2. dilute acid
R
OH
R′
C
CH₂N
H
H
hydroxynitrile
primary amine

Figure 5: *The general reaction for the reduction of a hydroxynitrile with $LiAlH_4$.*

Tip: Forming amines by reducing nitriles is useful if you just want the primary amine because you can't get further substitutions — the primary amine is the only product, unlike for nucleophilic substitution of a haloalkane with ammonia (see page 470).

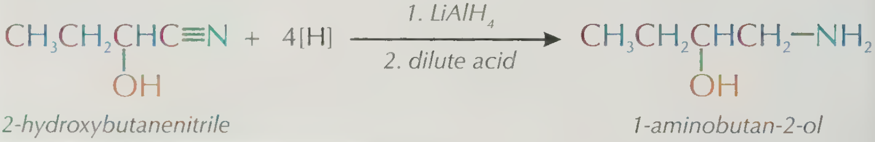
Examples

Here's the equation for the formation of ethylamine from ethanenitrile:

$$CH_3C{\equiv}N + 4[H] \xrightarrow[\text{2. dilute acid}]{\text{1. } LiAlH_4} CH_3CH_2NH_2$$

Ethanenitrile — *Ethylamine*

Here's the equation for the formation of 1-aminobutan-2-ol from 2-hydroxybutanenitrile:

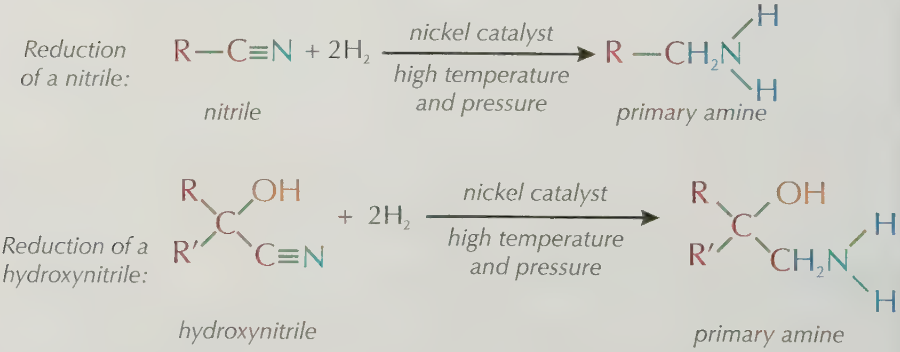


$$CH_3CH_2\underset{\displaystyle OH}{\underset{|}{C}}HC{\equiv}N + 4[H] \xrightarrow[\text{2. dilute acid}]{\text{1. } LiAlH_4} CH_3CH_2\underset{\displaystyle OH}{\underset{|}{C}}HCH_2{-}NH_2$$

2-hydroxybutanenitrile
1-aminobutan-2-ol

Tip: The prefix amino- tells you there's an amine group, just like the suffix -amine.

2. The method above is great in the lab, but $LiAlH_4$ is too expensive for industrial use. In industry, nitriles are reduced using hydrogen gas with a metal catalyst, such as platinum or nickel, at a high temperature and pressure — this is called catalytic hydrogenation. The general equations for the reduction of a nitrile or a hydroxynitrile are:



Reduction of a nitrile:
R—C≡N + 2H₂
nickel catalyst
high temperature and pressure
R —CH₂N
H
H
nitrile
primary amine
Reduction of a hydroxynitrile:
R
OH
R′
C
C≡N
+ 2H₂
nickel catalyst
high temperature and pressure
R
OH
R′
C
CH₂N
H
H
hydroxynitrile
primary amine

Figure 6: *The general reactions for the reduction of nitriles and hydroxynitriles with H_2 and a nickel catalyst.*

Hydrolysis of nitriles

If you reflux a nitrile in dilute hydrochloric acid, then the nitrile group will be hydrolysed to form a carboxylic acid. The carbon of the nitrile starting material becomes the carbon of the carboxyl group in the product.

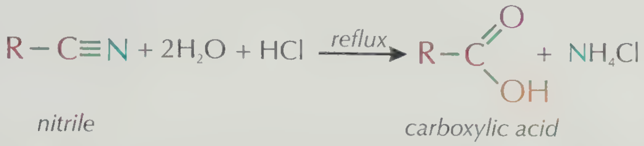


Figure 7: *The general reaction for the hydrolysis of a nitrile.*

Tip: Hydrolysis means using water to break up a compound. Here, the -C≡N bond reacts with water to break up and form -COO⁻ and NH_4^+.

You can do the same with a hydroxynitrile:

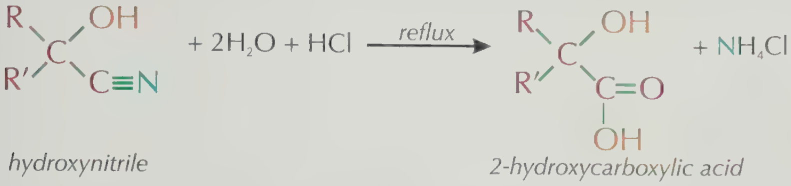
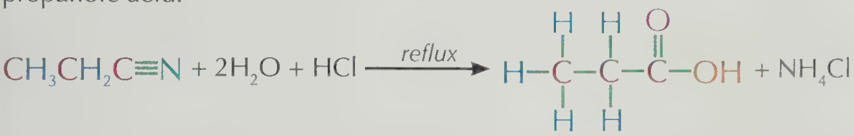


Figure 8: *The general reaction for the hydrolysis of a hydroxynitrile.*

Tip: The hydrochloric acid is diluted in water, so there are lots of water molecules in the mixture that can take part in these hydrolysis reactions.

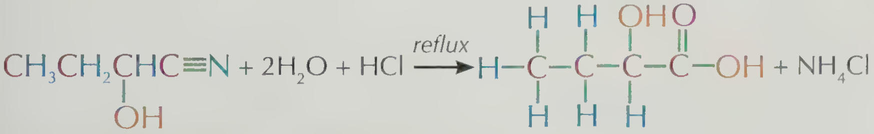
Examples

If you reflux propanenitrile with dilute hydrochloric acid, you form propanoic acid:



$$CH_3CH_2C{\equiv}N + 2H_2O + HCl \xrightarrow{reflux} H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\overset{O}{\overset{\|}{C}}-OH + NH_4Cl$$

If you reflux 2-hydroxybutanenitrile with dilute hydrochloric acid, you form 2-hydroxybutanoic acid:



$$CH_3CH_2\underset{OH}{CH}C{\equiv}N + 2H_2O + HCl \xrightarrow{reflux} H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{OH}{C}}-\overset{O}{\overset{\|}{C}}-OH + NH_4Cl$$

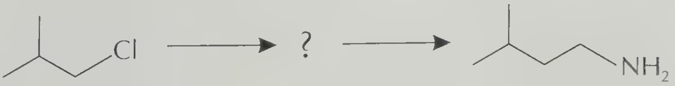
Using nitriles in synthetic routes

If the product of a synthesis reaction contains one more carbon in the chain than the starting compound had, then it's likely that the synthetic route will include formation of a nitrile or hydroxynitrile. It's possible the synthetic route will have two steps — the first to make the nitrile in order to extend the carbon chain, and the second to react the nitrile group and form a different functional group.

Tip: Nitriles can react to make lots of different functional groups, which makes them useful in synthesis.

Example

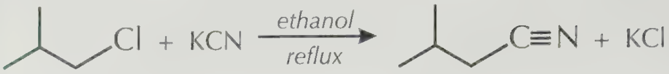
Plan a two-step synthetic route to synthesise 3-methylbutamine from 1-chloro-2-methylpropane. You should include all reagents and conditions, as well as showing any intermediate products.



The product has one more carbon than the starting compound, so the synthetic route must include formation of a new carbon-carbon bond. The starting compound is a chloroalkane so one way to form the new carbon-carbon bond is to react it with a cyanide ion in a nucleophilic substitution reaction to form a nitrile.

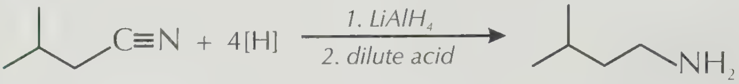
Tip: You could also use other cyanide compounds, such as NaCN or HCN, in the first step of this synthetic route.

The first step of the synthetic route is:



Cl
+ KCN
ethanol
reflux
C≡N
+ KCl

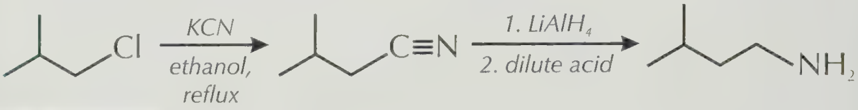
The nitrile can then be reduced to form a primary amine — and there's your product. So the second step could be:



C≡N
+ 4[H]
1. LiAlH₄
2. dilute acid
NH₂

Tip: There are other ways to reduce nitriles on page 494.

Overall the synthetic route is:



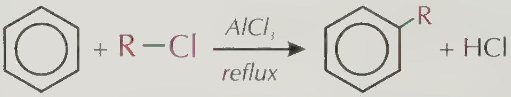
Cl
KCN
ethanol, reflux
C≡N
1. LiAlH₄
2. dilute acid
NH₂

Forming new C–C bonds to benzene rings

You can form new carbon-carbon bonds to benzene rings using Friedel-Crafts reactions. To do this, you reflux benzene with a halogen carrier (e.g. $AlCl_3$) and either a haloalkane or an acyl chloride. A new carbon-carbon bond is formed between the benzene ring and the halogenated carbon in the organic reactant. This is an electrophilic substitution reaction.

Tip: See pages 444-445 for more on Friedel-Crafts reactions.

If you use a haloalkane, you get Friedel-Crafts alkylation:

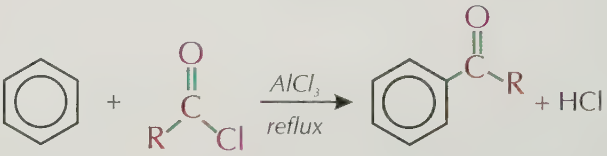


+ R—Cl
AlCl₃
reflux
R
+ HCl

Figure 9: *Friedel-Crafts alkylation reaction.*

Tip: 'Alkylation' means adding an alkyl group. 'Acylation' means adding an acyl (-COR) group.

If you use an acyl chloride, you get Friedel-Crafts acylation:



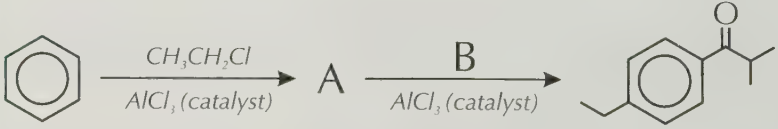
+
O
C
R
Cl
AlCl₃
reflux
O
C
R
+ HCl

Figure 10: *Friedel-Crafts acylation reaction.*

You may have to design a synthetic route that includes using a Friedel-Crafts reaction.

Example

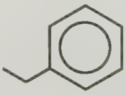
Consider the following reaction scheme:



CH₃CH₂Cl
AlCl₃ (catalyst)
A
B
AlCl₃ (catalyst)
O

What is A, the organic product of the first step?

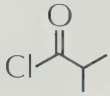
In the first step, benzene is reacted with chloroethane and a halogen carrier. It's a Friedel-Crafts alkylation reaction, so the product is ethylbenzene:



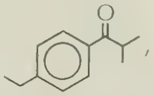
What is the reagent, B, in the second step?

Ethylbenzene (the product from the first step) is acylated in the second step, so the reaction will be a Friedel-Crafts acylation.

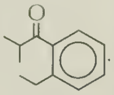
The reagent is 2-methylpropanoylchloride:



Tip: This reaction would give you a mixture of the desired product:



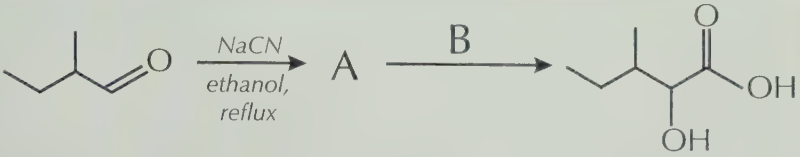
along with some of this side product:



You'd have to purify the reaction mixture after the reaction was finished in order to get a sample containing only the desired product.

Practice Questions — Application

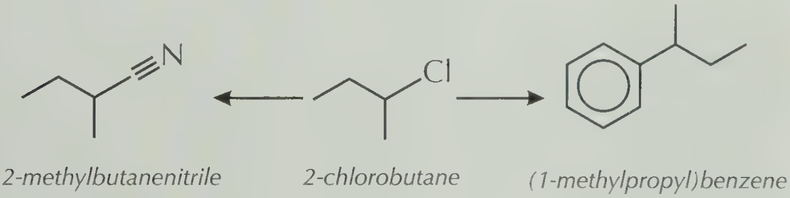
Q1 The following reaction scheme shows a route for synthesising 2-hydroxy-3-methylpentanoic acid from 2-methylbutanal.



a) Draw the skeletal formula of the organic compound, A, formed when 2-methylbutanal is heated under reflux with sodium cyanide in ethanol.

b) Give the reagents and conditions, B, that could be used to convert the organic product, A, into 2-hydroxy-3-methylpentanoic acid.

Q2 The reaction scheme below shows some reactions of 2-chlorobutane.



a) Give the reagents and conditions needed in the reaction that converts 2-chlorobutane to 2-methylbutanenitrile.

b) 2-methylbutanenitrile can be reduced using hydrogen and a nickel catalyst at high temperature and pressure. Draw the skeletal formula of the product of this reaction.

c) Give the reagents and conditions needed in the reaction to convert 2-chlorobutane to (1-methylpropyl)benzene.

Exam Tip
Make sure you give the right type of formula if you're asked for one in the exam (e.g. skeletal or displayed) — otherwise you might lose marks.

Practice Questions — Fact Recall

Q1 What type of reaction takes place when a haloalkane is heated under reflux with sodium cyanide in ethanol?

Q2 What type of compound is formed when a carbonyl compound reacts with hydrogen cyanide?

Q3 Name two reactions that could be used to form new carbon-carbon bonds with a benzene ring.

Learning Objective:

- Be able to describe and carry out the techniques and procedures used for the preparation and purification of organic solids involving use of a range of techniques including:
  (i) Organic preparation by distillation and heating under reflux using Quickfit apparatus.
  (ii) Purification of an organic solid using filtration under reduced pressure, recrystallisation and measurement of melting points (PAG 6).

Specification Reference 6.2.5

2. Practical Techniques in Organic Synthesis

PRACTICAL ACTIVITY GROUP 6

There was a whole host of techniques in Module 4: Section 3 for making and purifying organic liquids. Now it's time for organic solids. Making them is quite similar, but you can purify them in slightly different ways.

Preparation of organic substances

Organic reactions are slow and the substances are usually flammable and volatile (they've got low boiling points). If you stick them in a beaker and heat them with a Bunsen burner they'll evaporate or catch fire before they have time to react. You can reflux a reaction to get round this problem.

The mixture's heated in a flask fitted with a vertical Liebig condenser (see Figure 1) — so when the mixture boils, the vapours are condensed and recycled back into the flask. This stops reagents being lost from the flask, and gives them time to react.

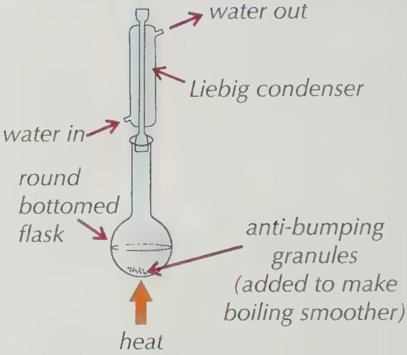


Figure 1: *Reflux apparatus.*

Tip: Have a look back at pages 279-280 if all this distillation and reflux business seems a bit hazy — it's all there in Module 4.

Tip: The glassware you use in organic synthesis is normally a type of Quickfit® apparatus. These are pieces of apparatus with ground glass joints that can be fitted together easily in a variety of different ways to form the set-up for a number of different techniques.

One problem with refluxing a reaction is that it can cause the desired product to react further. If this is the case you can carry out the reaction in a distillation apparatus instead. In distillation, the mixture is gently heated and substances evaporate out of the mixture in order of increasing boiling point. If you know the boiling point of your pure product, you can use the thermometer to tell you when it's evaporating, and therefore when it's condensing. If the product of a reaction has a lower boiling point than the starting materials then the reaction mixture can be heated so that the product evaporates from the reaction mixture as it forms. The starting materials will stay in the reaction mixture as long as the temperature is controlled.

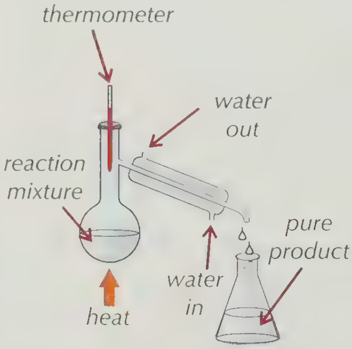


Figure 2: *Distillation apparatus.*

Filtration under reduced pressure

If your product is a solid, you can separate it from any liquid impurities by filtering it under reduced pressure. The reaction mixture is poured into a Büchner funnel with a piece of filter paper in it. The Büchner funnel is on top of a sealed sidearm flask which is connected to a vacuum line, causing it to be under reduced pressure. The reduced pressure causes suction through the funnel which causes the liquid to pass quickly into the flask, leaving behind dry crystals of your product.

Tip: See page 36 for more details on how to carry out a filtration under reduced pressure.

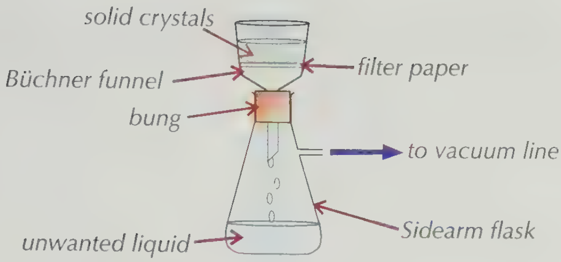


Figure 3: *Filtration apparatus.*

Recrystallisation

If the product of an organic reaction is a solid, then the simplest way of purifying it is a process called **recrystallisation**. Here's how it's done:

- Heat a suitable solvent on a hot plate or in a water bath. Slowly add the hot solvent to a flask containing the impure solid until the solid just dissolves and you have a saturated solution of the impure product. It's important not to add too much solvent, so add it a bit at a time, keep the flask you're adding it to warm (e.g. on a hot plate) and swirl it regularly.
- Once the solid has dissolved, you should filter the saturated solution to remove any solid impurities. You can do this by carrying out a filtration using fluted filter paper (see page 37 for how to do this). The filter funnel you use and the flask that the filtrate runs into should be warm to stop the saturated solution from cooling down too quickly.
- Once any solid impurities have been filtered out, you need to slowly cool the solution. Leave it to cool at room temperature first and then use an ice bath to cool it further. Crystals of the product will form as it cools. The impurities will stay in solution, as they are present in much smaller amounts than the product, so take much longer to crystallise out.
- If no crystals form when you cool your solution, it could be because you added too much solvent. You can evaporate off some of the excess solvent by putting the flask back on a hot plate or in a water bath. It could also be because there's nothing for the crystals to form on — they need a point to start from. A scratch on the glass container is usually enough, so try gently scratching the inside of the flask with a glass rod.
- Once the crystals have formed, you can separate them from the solution by filtration under reduced pressure. Wash the crystals left in the Büchner funnel with ice-cold solvent to rinse through any remaining solvent that may contain impurities, then leave the crystals to dry. You should have crystals of your product that are much purer than the original solid.

Choosing the solvent for recrystallisation

When you recrystallise a product, you must use an appropriate solvent for that particular substance. It will only work if the solid is very soluble in the hot solvent, but nearly insoluble when the solvent is cold. If your product isn't soluble enough in the hot solvent, you won't be able to dissolve it at all. If your product is too soluble in the cold solvent, most of it will stay in the solution even after cooling. When you filter it, you'll lose most of your product, giving you a very low yield. The impurities you want to remove from your product also need to be very soluble in the solvent when it is both hot and cold. This way, they'll stay in the solution as the product recrystallises, and be washed away when you carry out the filtration.

Figure 4: *The apparatus used to carry out a filtration under reduced pressure.*

Tip: Always carry out a risk assessment before you carry out any of the techniques on these pages.

Tip: In a saturated solution, the maximum possible amount of solid is dissolved in the solvent.

Tip: The more slowly the solution is cooled the larger the crystals will be. If you cool it too quickly the crystals could be so small that they'll pass through the filter paper and you'll struggle to separate them from the solution. Cooling too quickly can also cause the impurities to crystallise.

Tip: It's possible that not all of a product will recrystallise out of solution, so its yield will be reduced. But the crystals that do form will be really pure, which is often very important in things like drug synthesis.

Tip: Some capillary tubes are already sealed at one end, but some are open at both ends. If that's the case you'll need to seal it yourself. Just place the end of the capillary tube in a Bunsen flame at an angle of 45° and rotate it. You won't need to leave it in the flame for very long before it seals.

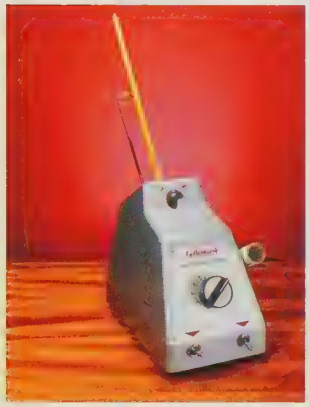


Figure 5: A melting point apparatus.

Tip: You could also use a piece of equipment called a Thiele tube to measure the melting point of a solid.

Sample	Melting point range (°C)
A	134-137
B	121-129
C	127-132

Figure 6: Melting points of three solids.

Testing the purity of an organic solid

Most pure substances have a specific melting and boiling point. If they contain impurities, the melting point's lowered and the boiling point is raised. If they're very impure, melting and boiling will occur across a wide range of temperatures. To accurately measure the melting point of an organic solid, you need to put a small amount of the solid in a capillary tube that's sealed at one end. To do this, put the solid in a watch glass and press the open end of the capillary tube into the substance. You should get a small 'plug' of the solid at the end of the tube. Turn the tube the other way up and tap it gently on a solid surface to knock the solid down to the bottom of the tube. Once you've done this, there are a couple of ways you can measure the melting point:

Examples

- Suspend the capillary tube in a beaker of oil with a very sensitive thermometer. Slowly heat the oil, with constant stirring, until the solid just begins to melt, and read the temperature on the thermometer. Wait until the solid has completely melted, and record the temperature on the thermometer again. This gives you the range of the melting point.
- You can also measure the melting point of a solid using a piece of equipment called a melting point apparatus (see Figure 5). The capillary tube and the thermometer are slotted into the machine which contains a metal block that is slowly warmed. There's a magnifying glass in front of the slot where the capillary tube is held, so you can spot exactly when the crystals start and finish melting.

Once you've measured the melting point of your sample, you can compare it to the known melting point of the substance to determine its purity. If the melting points are similar then your sample is quite pure, but if your value is much lower than the standard value, your sample contains impurities.

Practice Questions — Application

Q1 Use the table below to choose an appropriate solvent for the recrystallisation of benzoic acid. Explain your answer.

Solvent	Solubility of benzoic acid when solvent is hot	Solubility of benzoic acid when solvent is cold
Ethanol	Soluble	Soluble
Water	Soluble	Insoluble
Cyclohexane	Insoluble	Insoluble

Q2 Malik measures the melting points of three different samples of aspirin. In its pure form, aspirin has a melting point of 138-140 °C. Use the data in Figure 6 to put the samples A, B and C in order of increasing purity. Explain your answer.

Practice Questions — Fact Recall

Q1 What technique is used to heat an organic reaction mixture without losing any volatile substances?

Q2 What is filtration under reduced pressure used for when purifying an organic solid?

Q3 How could you test the purity of an organic solid?

3. Functional Groups and their Typical Reactions

Organic Chemistry is all about spotting functional groups and predicting how they'll react and what they'll form when they do react. Here's a summary of the reactions and functional groups in A Level Chemistry.

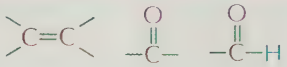
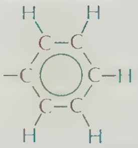
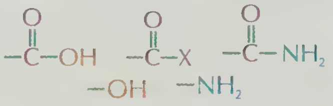
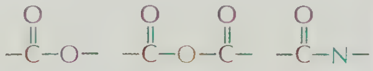
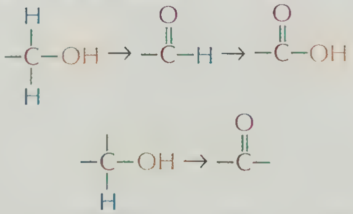
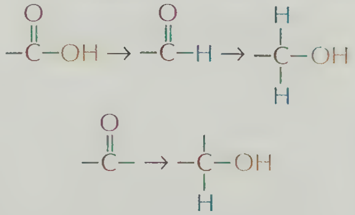
Learning Objectives:

- Be able to identify the individual functional groups in an organic molecule containing several functional groups.
- Be able to predict the properties and reactions of an organic molecule containing several functional groups.

Specification Reference 6.2.5

Types of reaction

In Organic Chemistry you can classify all the different reactions based on what happens to the molecules involved. All of the reactions you've met will fit into one of these seven types.

Reaction Type	Description	Examples of functional groups that undergo this type of reaction
Addition	Two molecules join together to form a single product. Involves breaking a double bond.	 $>C=C<$ $\quad -\overset{O}{\overset{\Vert}{C}}- \quad -\overset{O}{\overset{\Vert}{C}}-H$
Elimination / Dehydration	Involves removing a functional group which is released as part of a small molecule. Often, a double bond is formed. In dehydration, water is lost.	$-X$ *(X is a halogen. HX eliminated)* $-OH$ *(H_2O eliminated)*
Substitution	A functional group is swapped for a new one.	$-OH$ $-X$  *(H replaced)*
Condensation	Two molecules are joined together with the loss of a small molecule, e.g. water or HCl.	 $-\overset{O}{\overset{\Vert}{C}}-OH \quad -\overset{O}{\overset{\Vert}{C}}-X \quad -\overset{O}{\overset{\Vert}{C}}-NH_2$ $-OH \quad -NH_2$
Hydrolysis	Water is used to split apart a molecule, creating two smaller ones.	 $-\overset{O}{\overset{\Vert}{C}}-O- \quad -\overset{O}{\overset{\Vert}{C}}-O-\overset{O}{\overset{\Vert}{C}}- \quad -\overset{O}{\overset{\Vert}{C}}-N-$
Oxidation	Oxidation is the loss of electrons. In Organic Chemistry, it usually means gaining an oxygen atom or losing a hydrogen atom.	 $-\underset{H}{\overset{H}{C}}-OH \rightarrow -\overset{O}{\overset{\Vert}{C}}-H \rightarrow -\overset{O}{\overset{\Vert}{C}}-OH$ $-\underset{H}{C}-OH \rightarrow -\overset{O}{\overset{\Vert}{C}}-$
Reduction	Reduction is the gain of electrons. In Organic Chemistry, it usually means gaining a hydrogen atom or losing an oxygen atom.	 $-\overset{O}{\overset{\Vert}{C}}-OH \rightarrow -\overset{O}{\overset{\Vert}{C}}-H \rightarrow -\underset{H}{\overset{H}{C}}-OH$ $-\overset{O}{\overset{\Vert}{C}}- \rightarrow -\underset{H}{C}-OH$

Tip: Hydrolysis is the opposite reaction to condensation.

Tip: Polyesters and polyamides can be hydrolysed to their constituent monomers.

Tip: Reduction is the opposite reaction to oxidation.

Functional groups

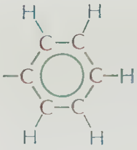
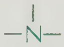
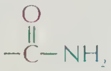
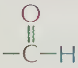
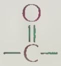
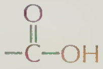
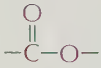
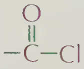
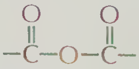
Functional groups are the parts of a molecule that are responsible for the way the molecule reacts. Substances are grouped into families called **homologous series** based on what functional groups they contain. Here's a round-up of all the ones you've studied:

Exam Tip
You need to learn all of these functional groups off by heart — they won't be given to you in the exam.

Tip: Aromatic compounds can also be called 'arenes'.

Tip: Amines are classed as primary, secondary, tertiary or quaternary ammonium ions depending on whether the nitrogen is bonded to one, two, three or four carbon atoms.

Tip: Amides can be classed as primary or secondary depending on whether the nitrogen is bonded to one or two carbon atoms.

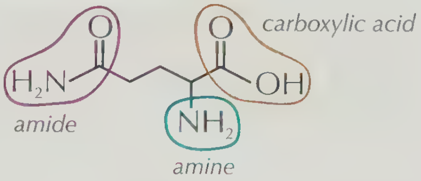
Homologous series	Functional group	Properties	Typical reactions
Alkane	only C–C and C–H	Non-polar, unreactive.	Radical substitution
Alkene	C=C	Non-polar, electron-rich double bond.	Electrophilic addition
Aromatic compounds		Stable delocalised ring of electrons.	Electrophilic substitution
Alcohol	–OH	Polar C–OH bond.	Nucleophilic substitution, dehydration/elimination
		Lone pair on oxygen can act as a nucleophile.	Esterification, nucleophilic substitution
Haloalkane	–X (X is a halogen)	Polar C–X bond.	Nucleophilic substitution, elimination
Amine	 $-\underset{}{\overset{|}{N}}-$	Lone pair on nitrogen can act as a base or a nucleophile.	Neutralisation, nucleophilic substitution
Amide	 $-\overset{\overset{O}{\|}}{C}-NH_2$	–	–
Nitrile	$-C{\equiv}N$	Electron deficient carbon centre.	Reduction, hydrolysis
Aldehyde	 $-\overset{\overset{O}{\|}}{C}-H$	Polar C=O bond.	Nucleophilic addition, reduction, oxidation
Ketone	 $-\overset{\overset{O}{\|}}{C}-$	Polar C=O bond.	Nucleophilic addition, reduction
Carboxylic acid	 $-\overset{\overset{O}{\|}}{C}-OH$	Electron deficient carbon centre.	Neutralisation, esterification
Ester	 $-\overset{\overset{O}{\|}}{C}-O-$	Electron deficient carbon centre.	Hydrolysis
Acyl chloride	 $-\overset{\overset{O}{\|}}{C}-Cl$	Electron deficient carbon centre.	Nucleophilic substitution, condensation (lose HCl), Friedel-Crafts acylation
Acid anhydride	 $-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-$	Electron deficient carbon centre.	Esterification

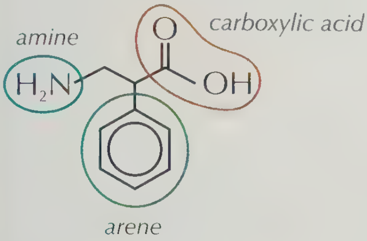
The functional groups in a molecule give you clues about its properties and reactions. For example, a -COOH group will (usually) make the molecule acidic and mean it will form esters with alcohols.

In the exam, you may be asked to identify all the functional groups in a molecule. There may be more than one, and you need to be able to recognise them all.

Examples

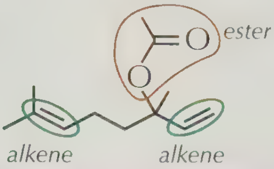
The molecule on the right has three functional groups: a carboxylic acid group, an amine group and an amide group.





The molecule on the left has three functional groups: a carboxylic acid group, an arene group and an amine group.

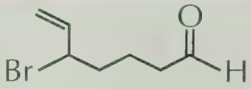
The molecule on the right has three functional groups: an ester group and two alkene groups.



Tip: A carboxylic acid group can also be called a 'carboxyl group'.

Practice Questions — Application

Q1 For the molecule on the right:

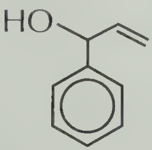


a) Name the functional groups.

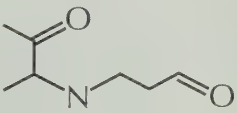
b) Explain why you might expect this molecule to undergo an oxidation reaction. What different functional group would the product of oxidation contain?

Q2 The molecules below all contain a variety of functional groups:

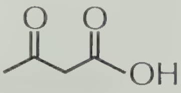
A:



B:



C:



a) Which of the molecules contain an alcohol group?

b) Which of the molecules would you expect to take part in condensation reactions?

c) Which of the molecules could take part in reduction reactions to form secondary alcohols?

Practice Questions — Fact Recall

Q1 Draw the displayed formula of each of these functional groups:

a) arene b) primary amine c) ester

Q2 Name these functional groups:

a) -C≡N b) $-CONH_2$ c) -CHO

Learning Objective:

- Be able to devise multi-stage synthetic routes for preparing organic compounds.

Specification Reference 6.2.5

4. Synthetic Routes

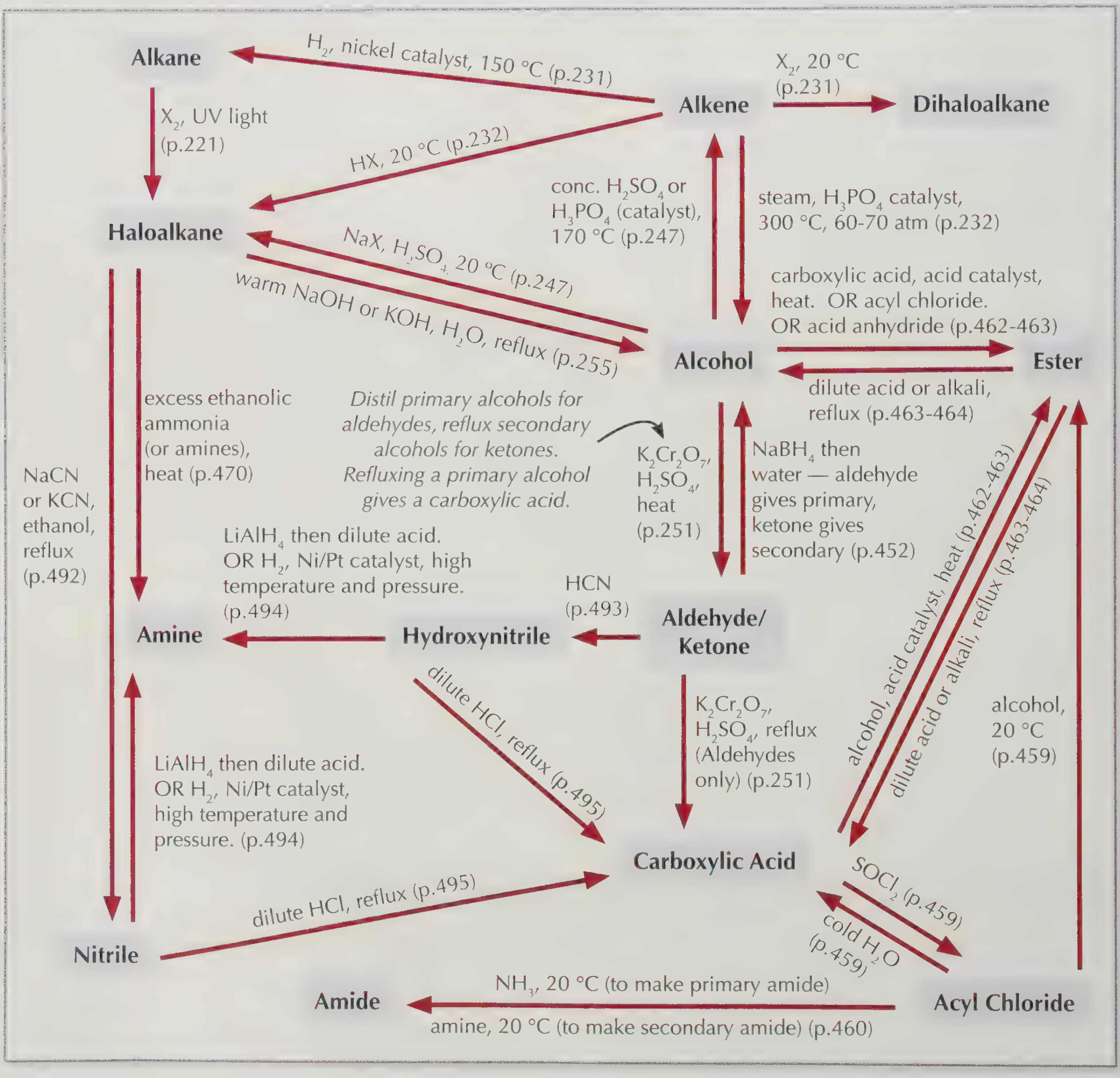
In your exam, you may be asked to suggest a pathway for the synthesis of a particular molecule. The pathway may contain more than one step. These pages contain a summary of some of the reactions you should know.

Devising synthetic routes

HOW SCIENCE WORKS

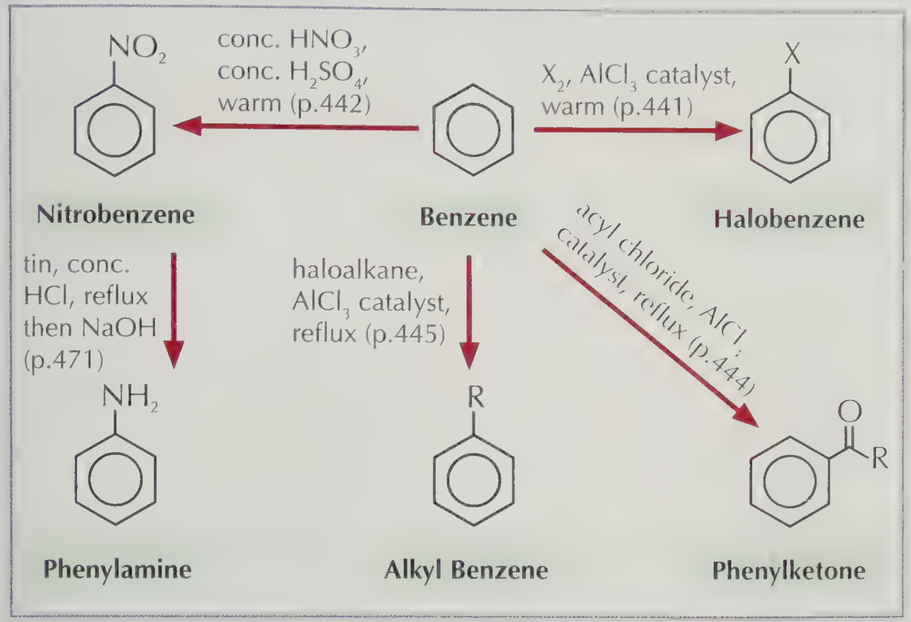
Chemists have got to be able to make one compound from another. It's vital for things like designing medicines. Chemists use **synthetic** routes to show the reagents, conditions and any special procedures needed to get from one compound to another. The reaction schemes on the next two pages show some of the synthetic routes you've come across in the A Level Chemistry course. These reactions are covered elsewhere in the book, so check back for extra details.

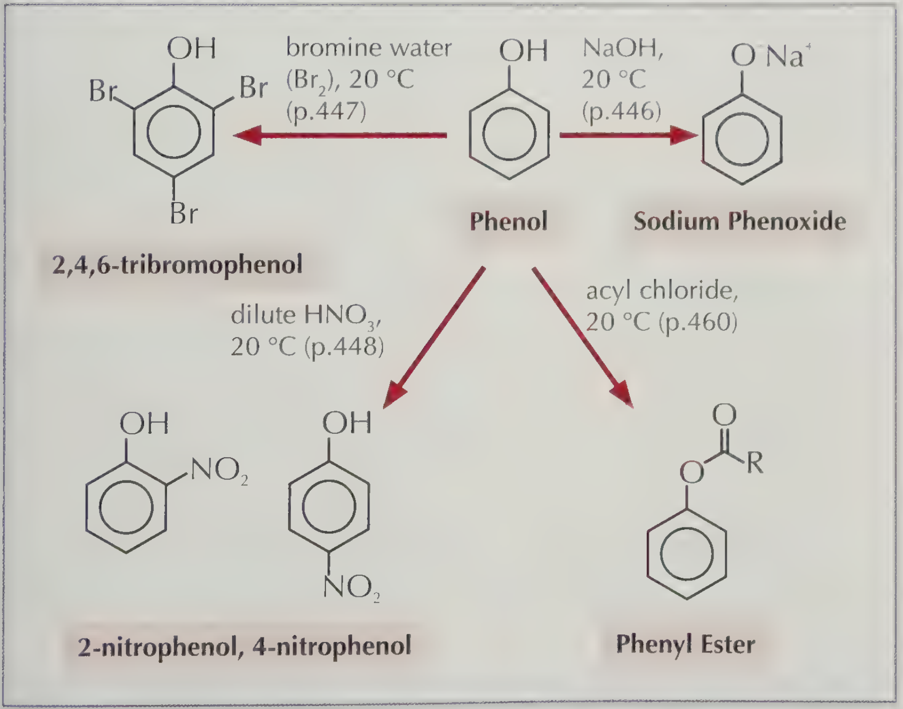
Synthesis routes for aliphatic compounds


Alkane
H_2, nickel catalyst, 150 °C (p.231)
Alkene
X_2, 20 °C (p.231)
Dihaloalkane
X_2, UV light (p.221)
HX, 20 °C (p.232)
conc. H_2SO_4 or H_3PO_4 (catalyst), 170 °C (p.247)
steam, H_3PO_4 catalyst, 300 °C, 60-70 atm (p.232)
Haloalkane
NaX, H_2SO_4, 20 °C (p.247)
warm NaOH or KOH, H_2O, reflux (p.255)
carboxylic acid, acid catalyst, heat. OR acyl chloride. OR acid anhydride (p.462-463)
Alcohol
Ester
dilute acid or alkali, reflux (p.463-464)
excess ethanolic ammonia (or amines), heat (p.470)
Distil primary alcohols for aldehydes, reflux secondary alcohols for ketones. Refluxing a primary alcohol gives a carboxylic acid.
$K_2Cr_2O_7$, H_2SO_4, heat (p.251)
$NaBH_4$ then water — aldehyde gives primary, ketone gives secondary (p.452)
NaCN or KCN, ethanol, reflux (p.492)
$LiAlH_4$ then dilute acid. OR H_2, Ni/Pt catalyst, high temperature and pressure. (p.494)
HCN (p.493)
Amine
Hydroxynitrile
Aldehyde/ Ketone
alcohol, acid catalyst, heat (p.462-463)
dilute acid or alkali, reflux (p.463-464)
alcohol, 20 °C (p.459)
dilute HCl, reflux (p.495)
$K_2Cr_2O_7$, H_2SO_4, reflux (Aldehydes only) (p.251)
$LiAlH_4$ then dilute acid. OR H_2, Ni/Pt catalyst, high temperature and pressure. (p.494)
Carboxylic Acid
$SOCl_2$ (p.459)
cold H_2O (p.459)
dilute HCl, reflux (p.495)
Nitrile
Amide
NH_3, 20 °C (to make primary amide)
amine, 20 °C (to make secondary amide) (p.460)
Acyl Chloride

Synthetic routes for aromatic compounds

There aren't so many of these reactions to learn — so make sure you know all the itty-bitty details. If you can't remember any of the reactions, look back to the relevant pages and take a quick peek over them.


NO2
conc. HNO3, conc. H2SO4, warm (p.442)
X2, AlCl3 catalyst, warm (p.441)
X
Nitrobenzene
Benzene
Halobenzene
acyl chloride, AlCl3 catalyst, reflux (p.444)
tin, conc. HCl, reflux then NaOH (p.471)
haloalkane, AlCl3 catalyst, reflux (p.445)
NH2
R
O
R
Phenylamine
Alkyl Benzene
Phenylketone


OH
Br
Br
bromine water (Br2), 20 °C (p.447)
OH
NaOH, 20 °C (p.446)
O⁻Na⁺
Br
Phenol
Sodium Phenoxide
2,4,6-tribromophenol
dilute HNO3, 20 °C (p.448)
acyl chloride, 20 °C (p.460)
OH
NO2
OH
NO2
O
O
R
2-nitrophenol, 4-nitrophenol
Phenyl Ester

Organic synthesis in the exam

In your exams, you could be asked to provide a step-wise synthesis for the production of one chemical from another. You might have to use any of the reactions mentioned on the previous two pages so it's really important that you learn them all really well.

Tip: If you do any of these synthesis reactions in class, remember to carry out a risk assessment first.

Exam Tip
When you're writing down step-wise syntheses in the exam don't forget to put the conditions as well as the reagents. You might lose marks if you don't.

Tip: Functional groups on side-chains attached to a benzene ring will normally react in the same way as they would if they were in an aliphatic compound (see the reactions on the previous page).

Exam Tip
There may be fewer reactions involving aromatic compounds but they're just as likely to come up in the exam as the reactions on the previous page — so make sure you learn both sets of synthetic routes.

If you're asked how to make one compound from another in the exam, include:

- The names and quantities of all the reagents needed.
- Any special procedures, such as refluxing.
- The conditions needed, e.g. high temperature or pressure, or the presence of a catalyst.
- Any safety precautions, e.g. if there are things like hydrogen chloride around, you really don't want to go breathing them in, so do the reaction in a fume cupboard.

HYDROCHLORIC
ACID DIL.
HC1

Figure 1: *Reagents are chemicals that can be taken from bottles or containers.*

Exam technique

In the exam you may be asked to 'identify' the name of a reagent used in a synthesis step. A reagent is just a chemical that can be used straight out of a bottle or container, for example, hydrochloric acid (HCl) or sodium hydroxide (NaOH). You must be really careful about this...

Example

Identify the reagent used to transform a bromoalkane into an alcohol.

Giving the reagent as OH^- in this case would be incorrect as you can't just take it out of a bottle. A correct answer would be, e.g. $NaOH_{(aq)}$.

Practice Questions — Application

Q1 Write down the reagents and conditions you would use to carry out the following organic syntheses.

a) Making ethanol from ethene using steam hydration.

b) Forming bromomethane from methane.

Q2 The following syntheses require two-steps. Write down the reagents and conditions you would use to carry out each step.

a) Creating propanal from 1-bromopropane.

b) Making methyl butanoate from butanal.

Q3 In an organic synthesis, benzene was heated with H_2SO_4 and HNO_3 to make an intermediate, X. A tin catalyst and HCl were then added and the mixture was refluxed before adding NaOH to make the overall product, Y. Identify X and Y.

Q4 Give a three-step synthesis of dibromoethane starting from ethanal. In your second synthesis step you should form ethene. For each step, give the reagents and conditions you would use to carry out the reaction.

Q5 Give a three-step synthesis of propanone starting from propene. In your first synthesis step you should form 2-bromopropane. For each step, give the reagents and conditions you would use to carry out the reaction.

Exam Tip

For questions like these you don't have to give the mechanisms or equations for the reactions.

Exam Tip

You need to be specific when you're talking about reagents in the exam. Make sure you write down exactly what you need to use — writing 'an alcohol' when you really mean 'ethanol' just won't get you all of the marks.

Practice Questions — Fact Recall

Q1 Name three types of organic compound that can react in one step to form a haloalkane.

Q2 Name three types of organic compound that you could synthesise from an aldehyde in one step.

Q3 Give the reagent and conditions you need in order to make a phenyl ester from phenol.

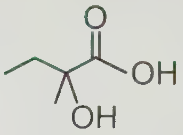
Section Summary

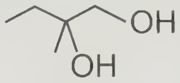
Make sure you know...

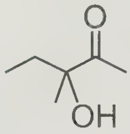
- That carbon-carbon bond formation is used in synthesis to increase the length of a carbon chain.
- That haloalkanes react with cyanide ions in ethanol in a nucleophilic substitution reaction to form nitriles, which results in the formation of a new C–C bond.
- The mechanism for the nucleophilic substitution reaction between haloalkanes and cyanide ions.
- That carbonyls, such as aldehydes and ketones, will react with hydrogen cyanide (HCN) in a nucleophilic addition reaction to form hydroxynitriles, which results in the formation of a new C–C bond.
- The mechanism for the electrophilic addition reaction between carbonyl compounds and hydrogen cyanide.
- How nitriles and hydroxynitriles can be reduced to form amines.
- How nitriles and hydroxynitriles can be hydrolysed with acid to form carboxylic acids.
- That Friedel-Crafts alkylation, using a haloalkane and a halogen carrier, can be used to form new C–C bonds to an aromatic ring.
- That Friedel-Crafts acylation, using an acyl chloride and a halogen carrier, can be used to form new C–C bonds to an aromatic ring.
- The techniques and procedures involved in preparing an organic compound, including using Quickfit apparatus, and the procedures for distillation and heating under reflux.
- How to purify an organic solid by filtration under reduced pressure.
- How to purify an organic solid by recrystallisation.
- How to check the purity of an organic solid by measuring its melting point.
- How to identify the functional groups in a molecule containing more than one functional group.
- How to predict the properties and reactions of an organic molecule based on its functional groups.
- How to devise multi-stage synthetic routes for preparing different organic compounds.

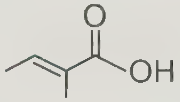
Exam-style Questions

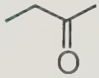
1 Which of the molecules, **A**-**D**, would not be a valid starting compound for synthesising the molecule shown on the right in two steps or fewer?



A 

B 

C 

D 

(1 mark)

2 A student is carrying out a recrystallisation to purify an organic solid.
Which of the following actions could result in the student getting a very low yield of the solid after recrystallisation?

Action 1: The student dissolved the solid in the smallest possible amount of hot solvent.

Action 2: The organic solid was soluble in the solvent when warm, but only partially soluble when cold.

Action 3: The student washed the crystals with some ice-cold solvent after filtering the recrystallised solid under reduced pressure.

A Actions 1, 2 and 3

B Only action 2

C Actions 2 & 3

D Only action 3

(1 mark)

3 Which of the following is not a valid two-step synthetic route?

A nitrile → amine → alcohol

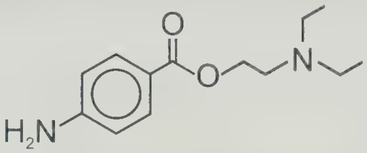
B hydroxynitrile → carboxylic acid → acyl chloride

C benzene → phenyl ketone → phenyl alcohol

D benzene → nitrobenzene → phenylamine

(1 mark)

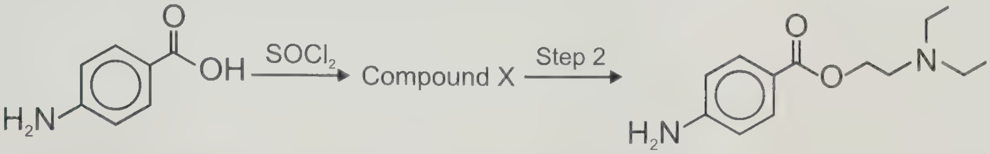
4 The drug procaine, shown below, is commonly used as a local anaesthetic.



(a) Redraw the structure of procaine, and circle and name all of the functional groups.

(2 marks)

(b) Procaine can be synthesised in two steps from 4-aminobenzoic acid. The reaction scheme is shown below, with some of the details missing.



(i) Draw the structure of Compound X, the organic product formed when 4-aminobenzoic acid is reacted with $SOCl_2$.

(1 mark)

(ii) Draw the reagent needed in Step 2 of the synthesis, and give the conditions needed for the reaction.

(2 marks)

(c) A chemist synthesises procaine in a laboratory. He measures the melting point of his final product, and finds it to be in the range of 48-53 °C. The recorded melting point of procaine is 61 °C.

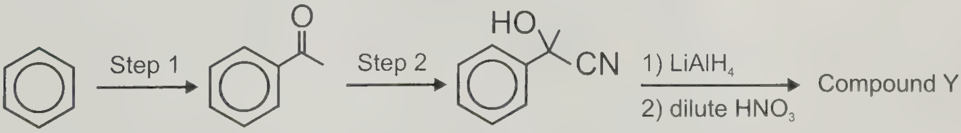
(i) What does the chemist's measured melting point for procaine tell you about his sample?

(1 mark)

(ii) Suggest one procedure the chemist could carry out that could improve the concordance between the melting point of his sample and the recorded value.

(1 mark)

5 The organic compound, Y, can be synthesised from benzene via the following three-stage reaction scheme:



(a) Name the reagents and conditions needed in Step 1 of the reaction scheme.

(1 mark)

(b) (i) Name the reagent(s) needed in Step 2 of the reaction scheme.

(1 mark)

(ii) Draw and name the mechanism for the reaction that occurs in Step 2.

(4 marks)

(c) Draw the structure of Compound Y.

(1 mark)

1. Tests for Organic Functional Groups

PRACTICAL ACTIVITY GROUP 7

Learning Objectives:

- Be able to qualitatively analyse organic functional groups on a test tube scale, and know the processes and techniques needed to identify specific organic functional groups in an unknown compound (PAG 7).
- Know how to identify alkenes by reaction with bromine (PAG 7).
- Know how to identify haloalkanes by reaction with aqueous silver nitrate in ethanol (PAG 7).
- Know how to identify phenols by weak acidity but no reaction with CO_3^{2-} (PAG 7).
- Know how to identify carboxylic acids by reaction with CO_3^{2-}.
- Know how to identify carbonyl compounds by reaction with 2,4-DNP (PAG 7).
- Know how to identify aldehydes by reaction with Tollens' reagent.
- Know how to identify primary and secondary alcohols and aldehydes by reaction with acidified dichromate (PAG 7).

Specification Reference 6.3.1

If you're given an unknown organic compound, there are several tests you can carry out to work out what it is. It's very important for each test to know what you're testing for, and how you will know if the result is positive. You've come across all of these tests already, but they're nicely summarised for you on the next few pages.

Testing for alkenes

To test whether an unknown compound is an alkene, you have to add bromine water. What you're actually testing for is unsaturation — the presence of double bonds (see page 440). Here's what you do:

1. Add 2 cm^3 of the substance that you want to test to a test tube.
2. Add 2 cm^3 of orange bromine water to the test tube.
3. Shake the test tube (see Figure 1) and watch what happens.

If the substance contains an alkene functional group, the solution will decolourise (go from orange, the colour of bromine water, to colourless). If there isn't an alkene present, nothing will happen.

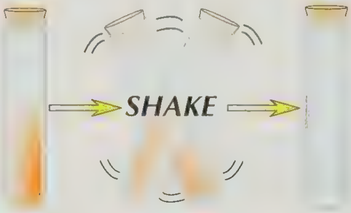


Figure 1: *Shaking a test tube containing an alkene and bromine water turns the solution from orange to colourless.*

Testing for haloalkanes

To test whether an unknown compound is a haloalkane, or contains a halogen, you have to add aqueous silver nitrate in ethanol. Here's how:

1. Add five drops of the unknown substance to a test tube.
2. Add 1 cm^3 of ethanol and 1 cm^3 of aqueous silver nitrate.
3. Place the test tube in a water bath to warm it.
4. Watch for a precipitate and observe the colour (see Figure 2).

Haloakane	Colour of precipitate
fluoroalkane	no precipitate forms
chloroalkane	white
bromoalkane	pale cream
iodoalkane	pale yellow

Figure 2: *Results of adding ethanol and aqueous silver nitrate to haloakanes.*

Tip: You may see aqueous silver nitrate called silver nitrate solution. Don't worry — they're the same thing.

Testing for phenols

Testing for phenols is a bit trickier, as you have to carry out a couple of reactions. What you're actually testing is the weak acidic nature of phenols (see page 446). First, you use the following method to test for a reaction with sodium hydroxide — sodium hydroxide is a strong base and so will react with any acid.

1. Add 2 cm^3 of the unknown substance to a test tube.
2. Add 1 small spatula of solid sodium hydroxide (or 2 cm^3 of sodium hydroxide solution).

If the substance contains an acid, such as a phenol, the solution will fizz and a colourless solution of a sodium salt will form. If the substance is not acidic, nothing will happen.

Next, you need to use the following test to see if the unknown substance will react with a carbonate — a much weaker base than sodium hydroxide. Carbonates will only react with strong acids, not weak acids such as a phenol.

1. Add 2 cm^3 of the unknown substance to a test tube.
2. Add 1 small spatula of a solid carbonate or 2 cm^3 of a carbonate solution (sodium carbonate will work nicely).

If the substance contains a phenol, nothing will happen. If the substance contains a strong acid, the solution will fizz as carbon dioxide gas is released.

Tip: Before carrying out any of the tests on these pages, you need to think about any safety issues that might be involved.

Tip: To confirm the presence of a phenol, you need it to react with NaOH, but not Na_2CO_3.

Tip: This second test forms the basis for the test to identify carboxylic acids (see below).

Testing for carboxylic acids

Unlike phenols, carboxylic acids do react with carbonates to form a salt, carbon dioxide and water (see page 458). The general equation for this reaction, using solid sodium carbonate, is:

$$2RCOOH_{(aq)} + Na_2CO_{3\,(s)} \rightarrow 2RCOO^-Na^+_{(aq)} + CO_{2\,(g)} + H_2O_{(l)}$$

You can use this reaction to test whether a substance is a carboxylic acid. Here's what to do:

1. Add 2 cm^3 of the substance that you want to test to a test tube.
2. Add 1 small spatula of a solid carbonate (or 2 cm^3 of a carbonate solution) e.g. sodium carbonate.
3. If the solution begins to fizz, bubble the gas that it produces through some limewater in a second test tube (see Figure 4).

If the unknown compound contains a carboxylic acid, the solution will fizz as carbon dioxide gas is produced. When you bubble carbon dioxide through limewater, the limewater turns cloudy.

If there isn't a carboxylic acid present, the limewater will stay colourless — you may not get a reaction at all.

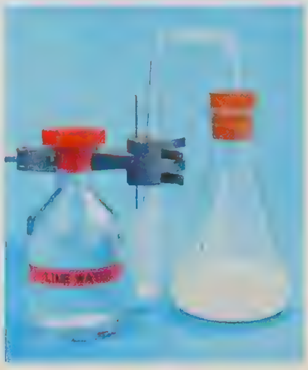


Figure 3: *A set-up used to test for carboxylic acids with carbonate ions and limewater.*

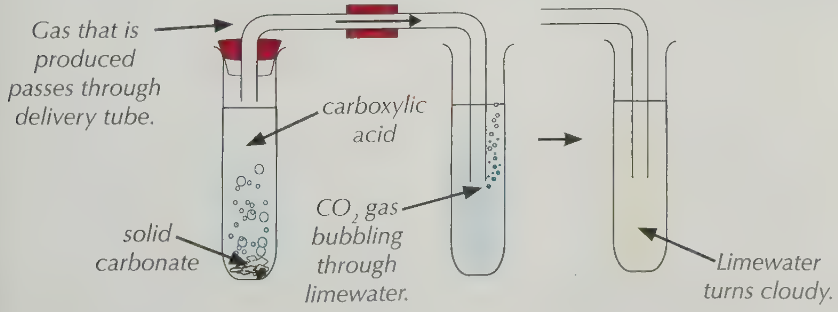

Gas that is produced passes through delivery tube.
carboxylic acid
solid carbonate
CO_2 gas bubbling through limewater.
Limewater turns cloudy.

Figure 4: *The test for identifying carboxylic acids.*

Tip: In this test, you need to make sure the reaction vessel is airtight, and the only place the gas can escape is through the tube that leads to the test tube containing limewater.

Tip: You may sometimes see 2,4-DNPH called 2,4-DNP.

Tip: The solution you've made at the end of step 1 is known as Brady's reagent.

Exam Tip
You won't need to remember specific quantities and concentrations for the exams — just make sure you know the reagents, the method and the expected observations.

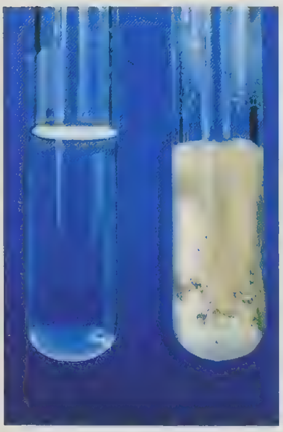


Figure 5: The colourless solution in the test tube on the left shows the unreacted Tollens' reagent. The test tube on the right shows the result of a reaction with an aldehyde.

Tip: Aldehydes and ketones are flammable, so the test tube should be heated in a water bath, rather than over a flame. See pages 33-34 for more on heating methods that don't involve naked flames.

Testing for aldehydes and ketones

With this test, you need to use the reagent 2,4-dinitrophenylhydrazine (2,4-DNPH). It may be a bit of a mouthful to say, but it's great for testing for aldehydes and ketones (see page 455).

1. Dissolve 0.2 g of 2,4-DNPH in 1 cm^3 of sulfuric acid, 2 cm^3 of water and 5 cm^3 of methanol.
2. In a different test tube, add 5 drops of the unknown substance to 2 cm^3 of your solution from step 1.
3. Shake the test tube and watch for a precipitate.

If the unknown compound is an aldehyde or a ketone, the 2,4-DNPH will react with the carbonyl group and a bright orange precipitate will form. If there isn't an aldehyde or ketone group present, nothing will happen.

Testing for aldehydes

This is another test for carbonyls (see above) but this time, it allows you to tell aldehydes and ketones apart. Unfortunately you have to prepare the reagent yourself. Mean.

1. Put 2 cm^3 of 0.10 mol dm^{-3} silver nitrate solution in a test tube.
2. Add 5 drops of 0.80 mol dm^{-3} sodium hydroxide solution. A light brown precipitate should form.
3. Add drops of dilute ammonia solution until the brown precipitate dissolves completely. You have now prepared the reagent known as Tollens' reagent (see Figure 6).
4. Add 10 drops of aldehyde or ketone and place the test tube in a warm water bath. Wait for a few minutes (see Figure 7).

If the substance contains an aldehyde, a silver mirror (a thin coating of silver) forms on the walls of the test tube (see Figures 5 and 7). There's no reaction with other carbonyls, such as ketones.

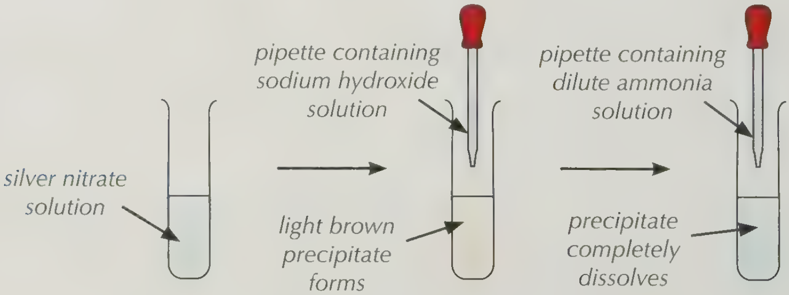

silver nitrate solution
pipette containing sodium hydroxide solution
light brown precipitate forms
pipette containing dilute ammonia solution
precipitate completely dissolves

Figure 6: *Preparing Tollens' reagent.*

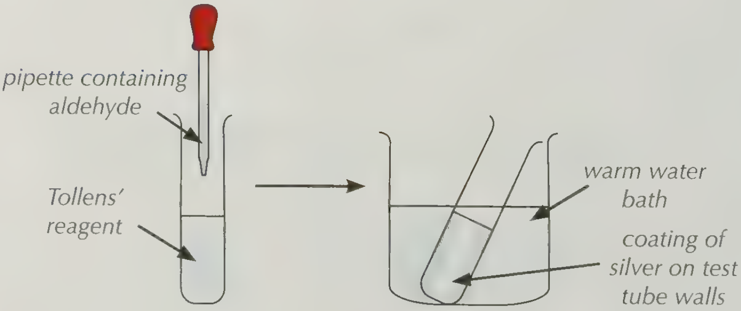

pipette containing aldehyde
Tollens' reagent
warm water bath
coating of silver on test tube walls

Figure 7: *Using Tollens' reagent to identify the presence of an aldehyde.*

Testing for primary and secondary alcohols

This test allows you to test for the presence of primary or secondary alcohols, but doesn't distinguish between them. Here's how:

1. Add 10 drops of the unknown substance to 2 cm³ of acidified potassium dichromate(VI) solution in a test tube.
2. Warm the mixture gently in a water bath and watch for a colour change.

If a primary or secondary alcohol is present, the orange solution slowly turns green (see Figures 8 and 9). If a tertiary alcohol is present, nothing will happen.

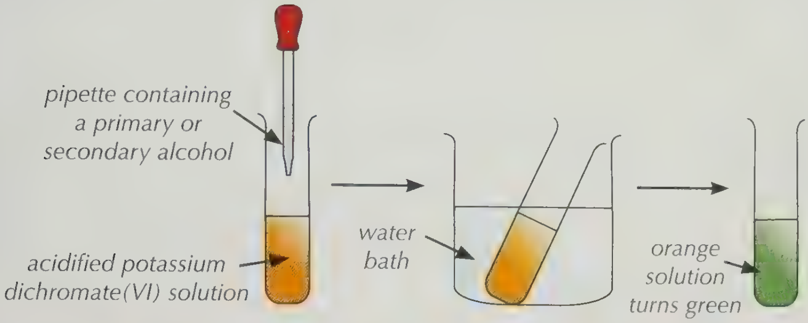

pipette containing a primary or secondary alcohol
acidified potassium dichromate(VI) solution
water bath
orange solution turns green

Figure 9: *Testing for primary and secondary alcohols.*

Practice Questions — Application

Q1 A student has an unknown organic compound. They add it to a test tube containing a solution of ethanol and aqueous silver nitrate. They warm the test tube for a while, and a pale cream precipitate forms. What functional group does the unknown compound contain?

Q2 A student has three test tubes. Each test tube contains one of three organic compounds: propanal, propanoic acid and propanone. Outline a series of tests the student could carry out to identify which test tube contains which compound. You should include details of any reagents, conditions and expected observations.

Q3 A student is investigating the behaviour of primary alcohols.

- a) She firstly adds a primary alcohol to a solution containing acidified potassium dichromate(VI) ions.
  What colour change would you expect her to see?
- b) She then adds a spatula of calcium carbonate to the resulting solution. The solution starts to fizz. The student bubbles the resulting gas through a test tube containing limewater.
  What would you expect the student to observe?

Practice Questions — Fact Recall

Q1 What reagent would you add to an unknown substance to test whether it contained an alkene?

Q2 What colour precipitate would you expect to form if you added aqueous silver nitrate to a test tube containing iodopropane?

Q3 Describe how you would test a sample of a compound to find out if it contained a phenol.

Q4 Describe what you would see if you added 2,4-dinitrophenylhydrazine to a solution containing a substance with a carbonyl group.

Tip: Primary alcohols are oxidised to aldehydes and then to carboxylic acids. Secondary alcohols are oxidised to ketones.

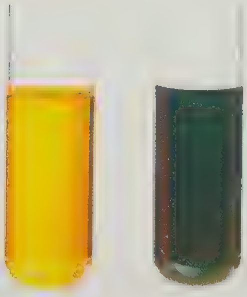


Figure 8: *The orange solution in the test tube on the left shows the unreacted acidified potassium dichromate. The test tube on the right shows the result of a reaction with a primary or secondary alcohol.*

Tip: The colour change is the orange dichromate(VI) ion ($Cr_2O_7^{2-}$) being reduced to the green chromium(III) ion (Cr^{3+}).

Tip: Qualitative analysis is a vital part of organic chemistry. It involves using tests, such as the ones outlined on these pages, to work out what functional groups are present in a compound. These tests are used by research scientists for identifying unknown compounds or confirming the identity of a product in organic synthesis.

HOW SCIENCE WORKS

2. Chromatography

Chromatography is used to separate and identify chemicals in mixtures.

Learning Objective:

- Be able to interpret one-way TLC chromatograms in terms of R_f values (PAG 6).

Specification Reference 6.3.1

The basics

Chromatography is used to separate different substances in a mixture — once the mixture's separated out, you can often identify the components, for example, different organic compounds. There are quite a few different types of chromatography (you might have tried paper chromatography already) but the ones you need to know about are thin-layer chromatography (TLC) and gas chromatography (GC) — there's more about GC in the next topic.

Tip: Before carrying out any chromatography experiment, you need to do a risk assessment.

Thin-layer chromatography

PRACTICAL ACTIVITY GROUP 6

In **thin-layer chromatography** (**TLC**) a solvent, such as ethanol, moves over a glass or plastic plate which is covered in a thin layer (0.1-0.3 mm thick) of solid, e.g. silica gel or aluminium powder. Here's how you separate a mixture using TLC:

1. Draw a pencil line near the bottom of the plate — this is called the base line. Put a spot of the mixture to be separated on the line.
2. Put the plate in a beaker containing a small amount of solvent — the level of solvent should cover the bottom of the plate, but not the spot.
3. Put a watch glass over the top of the beaker (this stops the solvent from evaporating). As the solvent spreads up the plate, the different substances in the mixture move with it, but different distances — so they separate out.
4. When the solvent's nearly reached the top, take the plate out of the beaker and mark the distance that the solvent has moved (the **solvent front**) in pencil.

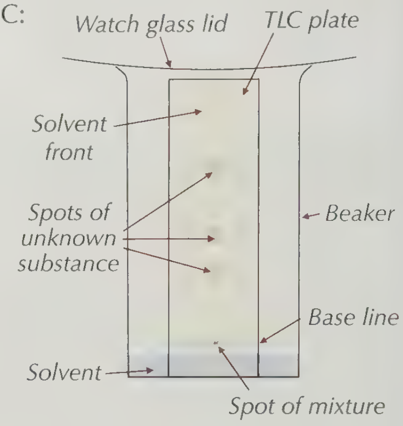


***Figure 2:** A thin-layer chromatography plate.*

Then you can leave the plate in a safe place to dry out before you analyse it. The plate, with its pattern of spots, is called a **chromatogram** (see Figure 1).

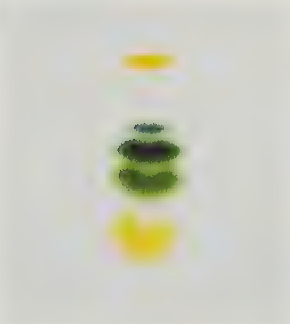


***Figure 1:** A TLC chromatogram.*

Tip: If the chemicals in your mixture are colourless, you'll have to treat the dried plate with a chemical like iodine or ninhydrin to make the spots visible.

R_f values

An **R_f value** is the ratio of the distance travelled by a spot to the distance travelled by the solvent. You can calculate them using this formula:

$$R_f \text{ value} = \frac{\text{distance travelled by spot}}{\text{distance travelled by solvent}}$$

Tip: R_f stands for 'retardation factor'.

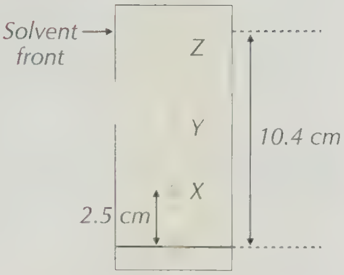
Tip: The distance travelled by the solvent is the distance between the base line and the solvent front.

When you're measuring how far a spot has travelled, you just measure from the base line (point of origin) to the vertical centre of the spot.

You can work out what was in a mixture by calculating an R_f value for each spot on the TLC plate and comparing your experimental values to the R_f values of known substances in a data book. This isn't always accurate as R_f values are affected by external conditions and changes in the set-up of the plate (see the next page) so it's good to run a pure sample of what you think your unknown is, alongside your unknown, to double-check.

Example — Maths Skills

A sugar solution containing a mixture of three sugars is separated using TLC. The chromatogram is shown on the right.



a) Calculate the R_f value of spot X.

To find the R_f value of spot X all you have to do is stick the numbers into the formula:

$$R_f \text{ value} = \frac{\text{distance travelled by spot}}{\text{distance travelled by solvent}}$$

$$= 2.5 \text{ cm} \div 10.4 \text{ cm} = 0.24$$

b) Figure 3 shows the R_f values of three sugars under the conditions used in the experiment. Use the table to identify the sugar present in spot X.

Spot X has an R_f value of 0.24. Fructose also has an R_f value of 0.24. So fructose is the sugar present in spot X.

Sugar	R_f value
Glucose	0.20
Fructose	0.24
Xylose	0.30

Figure 3: *R_f values of sugars.*

Factors affecting R_f values

How far an organic molecule travels up the plate depends on how strongly it's attracted to the layer of solid on the surface of the plate. The attraction between a substance and the solid surface of the plate is called **adsorption**. A substance that is strongly adsorbed will move slowly, so it won't travel as far as one that's only weakly adsorbed. This means it will have a smaller R_f value. Chemical properties, such as polarity, affect how strongly adsorbed a particular substances is to the plate.

The distance a particular substance moves up the plate also depends on the solid coating on the plate, the solvent used, and other external variables such as temperature. This means small changes in the TLC set-up, or the room you carry out your experiment in, can cause changes in the R_f value. So, once you've identified what you think an unknown compound is, it's best to check you're right by running a pure sample of the known substance alongside your unknown compound on a TLC plate. Identical substances should travel the same distance up the plate, i.e. have the same R_f value, as long as all other variables are controlled.

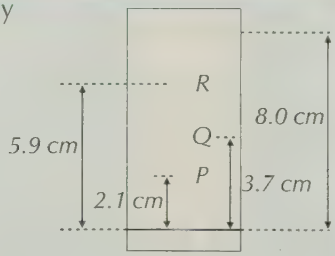
Exam Tip

Being able to use thin-layer chromatography to analyse organic compounds is a great example of How Science Works.

Tip: If you're given a drawing of a TLC plate that's to scale, you can use a ruler to measure the distances between the base line, the solvent front and the spots.

Practice Question — Application

Q1 A student used thin-layer chromatography to separate out a mixture of three amino acids. The chromatogram that she produced is shown on the right.



a) Calculate the R_f values of the three spots, P, Q and R.

b) Use the table in Figure 4 to identify the amino acid present in each spot.

c) Apart from using Figure 4, how could the student confirm that each amino acid has been identified correctly?

Tip: R_f values are always between 0 and 1.

Amino acid	R_f value
Glycine	0.26
Alanine	0.39
Tyrosine	0.46
Valine	0.61
Leucine	0.74

Figure 4: *R_f values of amino acids.*

Practice Questions — Fact Recall

Q1 Explain why mixtures separate during thin-layer chromatography.

Q2 Give the formula for calculating R_f values.

Q3 Name two things that can affect the R_f value of a certain compound.

3. Gas Chromatography

Learning Objective:

- Be able to interpret gas chromatograms in terms of retention times, and the amounts and proportions of the components in a mixture.

Specification Reference 6.3.1

The second type of chromatography you need to know about is gas chromatography. It's more high-tech than thin-layer chromatography, but the idea's just the same — things separating so you can identify them.

What is gas chromatography?

If you've got a mixture of volatile liquids (ones that turn into gases easily), then **gas chromatography** (GC) is the way to separate them out so that you can identify them. In gas chromatography, the sample to be analysed is injected into the machine, where it is vaporised (turned into a gas). A stream of carrier gas carries the sample through a coiled tube coated with a viscous liquid (such as an oil) or a solid.

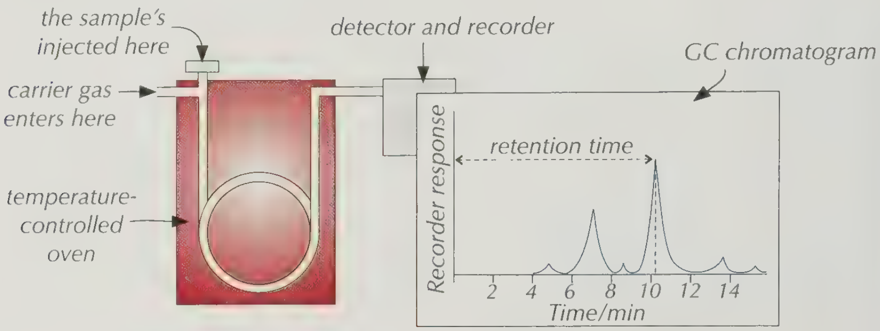


Figure 1: *Gas chromatography equipment and a chromatogram.*

Exam Tip
If you're writing about gas chromatography where the tube is coated in a liquid, then solubility is the word you need to use. If the tube is coated in a solid, you need to use adsorption — just like in TLC (see page 515-516).

If the tube is coated in liquid, the components of the mixture will constantly dissolve in it, evaporate into the gas, and then redissolve as they travel through the tube. The solubility of each component of the mixture determines how long it spends dissolved in the liquid and how long it spends moving along the tube in the gas. A substance with a high solubility will spend more time dissolved, so will take longer to travel through the tube to the detector than one with a lower solubility.

If the tube is coated in a solid, then the separation works in the same way as thin-layer chromatography (see page 515). How long each part of the mixture takes to travel through the tube will depend on how strongly it is adsorbed to the solid.

The time taken for the substances to pass through the coiled tube and reach the detector is called the **retention time**. It can be used to help identify the substances present in the mixture (see below).

Gas chromatograms

A gas **chromatogram** is a graph showing a series of peaks at the times when the detector senses something other than the carrier gas leaving the tube. They can be used to identify the substances within a sample and their relative proportions.

Each peak on a chromatogram corresponds to a substance with a particular **retention time**. Retention times are measured from zero to the centre of each peak, and can be looked up in a reference table, to identify the substances present.

Tip: Changes in the environment and in the set-up of your gas chromatography equipment affect retention times. This means reference values may not always match experimental ones you collect (see next page).

The area under each peak is proportional to the relative amount of each component that's present in the mixture (see Figure 2). For example, if a peak has three times the area of another peak, it tells you that there is three times as much of the first substance in the mixture (compared to the second substance).

Tip: If you're looking at the amount of each compound present, it's the area of the peaks (not the height) that's important — the tallest peak won't always represent the most abundant substance.

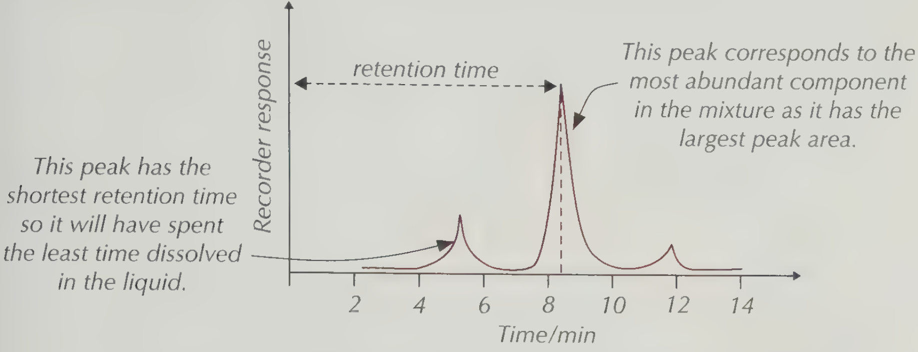


Figure 2: *A gas chromatogram showing the separation of three components in a mixture.*

You can calculate the proportion of a component in a mixture by comparing the area under its peak on a gas chromatogram, to the total area under all the peaks on the chromatogram. You can use this formula to do this:

$$\text{Percentage in original mixture} = \frac{\text{area of peak}}{\text{total area of all peaks}}$$

Retention times

You can use retention times to identify the components of a mixture. By comparing experimental retention times to retention times from reference tables and data books, you can work out the likely identity of an unknown compound. If you wanted to know if a mixture contained octane, you could run a sample of the mixture through the system, then look up the retention time for octane run under those conditions and see if it's the same as the retention time for a peak in your GC spectrum.

Tip: You could also run gas chromatography on a pure sample of what you think the unknown substance is and then compare the retention times.

If you're looking up retention times in a reference table, you must make sure that the conditions under which you did your experiment were the same as the conditions used when the data in the reference table was collected (e.g. at the same temperature).

There are several factors that affect retention times:

- Solubility or adsorption — this determines how long each component of the mixture spends in the stationary phase, and how long they spend moving along the tube in the gas. If the stationary phase is a liquid, then the more soluble a substance is, the more time it will spend dissolved. If the stationary phase is a solid, then the more strongly a substance is attracted to the solid, the more time it will spend adsorbed on the surface. It will therefore take longer to travel through the tube to the detector than one that is less soluble or less strongly adsorbed.
- Boiling point — a substance with a high boiling point will spend more time condensed as a liquid in the tube than as a gas. This means it will take longer to travel through the tube than one with a lower boiling point.
- Temperature of the gas chromatography instrument — a high temperature means the substance will spend more time evaporated in the gas and so will move along the tube quickly. It shortens the retention time for all the substances in the tube.

Tip: Adsorption is to do with how well a substance is attracted to the surface of a solid. Solubility is to do with how well something dissolves in a liquid. Make sure you use the right term depending on whether the stationary phase is a solid or a liquid.

Figure 3: *A researcher using a gas chromatograph to separate and identify the chemicals in a sample.*

External calibration curves

The area under the peak of a GC chromatogram gives you the relative amount of a substance, but finding the exact concentration is a bit trickier. To work out the concentration of a particular substance in a sample, you need create an **external calibration curve**. Fortunately it's not too hard — just follow these steps.

1. First, create a series of standard solutions of different concentrations of analyte — this is the substance you've chosen to detect for your calibration.
2. One by one, inject your standard solutions into a gas chromatography instrument and record the result.
3. For the chromatogram of each standard solution, calculate the area under the peak that corresponds to the analyte.
4. Plot these area values on a graph of area against concentration and then draw a line of best fit to create an external calibration curve.

It's a good idea to run a blank when you're making a calibration curve. A blank is just a solution containing all the solvents and reagents used when making the standard solutions, but no analyte. By subtracting the chromatogram of the blank from each of the chromatograms of your standard solutions, you can find a corrected peak value — one that takes into account the effect of reagents and solvents on the peak areas.

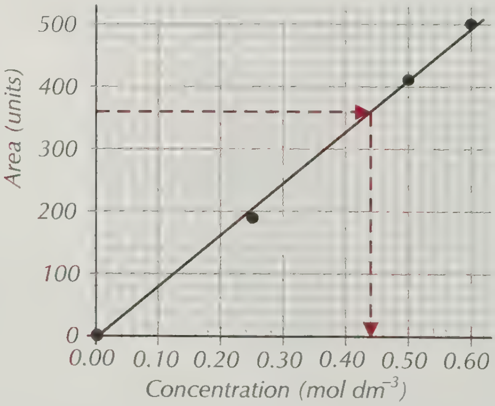
Your calibration curve is now ready to use — by reading along to the line of best fit, you can work out the concentration that corresponds to the area of a peak.

Example **Maths Skills**

On a chromatogram, the area under the peak for substance X is 360 units. Estimate the concentration of substance X in the sample by drawing an external calibration curve, using the data in the table below.
The areas have been corrected using a blank.

Concentration (mol dm^{-3})	0.00	0.25	0.50	0.60
Area (units)	0	190	410	500

First, plot the points from the table on a graph. Concentration is always plotted on the *x*-axis and area on the *y*-axis. Then draw a line (or curve) of best fit through your data set.



Now work out what concentration corresponds to an area of 360 units by drawing a line from 360 on the *y*-axis to where it meets the curve, and then drawing a line from this point down to the *x*-axis.
Read off the result on the *x*-axis.
So the concentration of substance X is **0.44 mol dm^{-3}**.

Exam Tip
Don't worry if the points you plot make a curve instead of a line. Just draw a curve that fits most of the points (a line of best fit) and read off the values in the same way.

Tip: Your calibration curve can be a straight line or a curve.

Tip: If you need the integration values for the areas of gas chromatography peaks in the exams, you'll be given them — you don't need to know how to work them out.

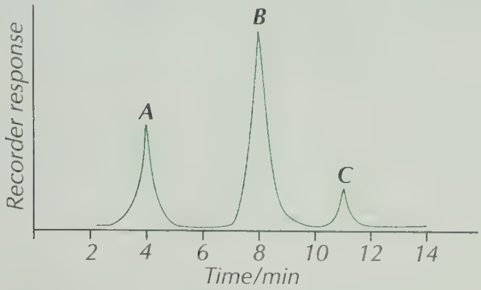
Tip: You can't just use one calibration curve for every gas chromatography experiment you ever do. As with retention times, calibration curves vary depending on external conditions and the set-up of your gas chromatography equipment.

Practice Questions — Application

Q1 A scientist is using gas chromatography to purify an organic product. She knows that the pure product is more soluble in the oil than the impurities. Will the pure product reach the detector before or after the impurities? Explain your answer.

Tip: Gas chromatography is a really popular method amongst scientists for working what unknown substances a mixture might contain.

Q2 Below is a gas chromatogram for a mixture of three components.



a) State which peak, A, B or C, corresponds to the component that spends the highest proportion of its time in the tube evaporated in the carrier gas.

b) One component of the mixture is hexene. Run under the same conditions, pure hexene has a retention time of 8 minutes. Which of the components, A, B or C, is hexene?

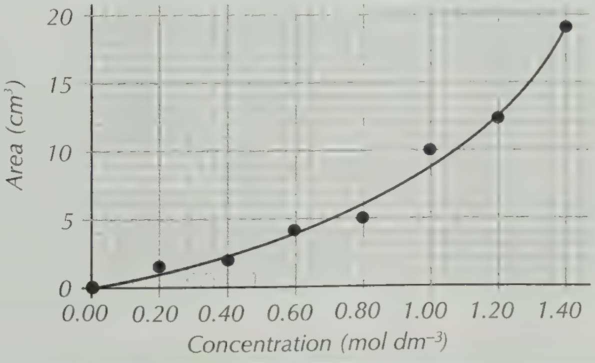
c) The smallest proportion of the mixture is made up of decene. Which of the components, A, B or C, is decene?

Exam Tip
Remember, in your exam answers it's 'retention time' that you need to talk about for gas chromatography and 'R_f value' for thin-layer chromatography — don't get them mixed up.

Q3 A gas chromatogram has two peaks.
Peak 1 has an area of 32 cm^2, and Peak 2 has an area of 16 cm^2.

a) Given that the only responses on the chromatogram were Peak 1 and Peak 2, what percentage of the original mixture was made up of the chemical that caused Peak 2?

b) Below is an external calibration curve for a chemical, X, that caused Peak 2. Estimate the concentration of X in the sample.



Exam Tip
In the exam, you may have to create your own calibration curve by plotting a graph.

Practice Questions — Fact Recall

Q1 Briefly explain why the components in a mixture separate out during gas chromatography when oil is used to coat the coiled tube.

Q2 What is retention time a measure of?

Q3 What does the area under each peak on a gas chromatogram tell you?

Q4 Describe how you could create an external calibration curve to work out the concentration of a substance.

4. NMR Spectroscopy

NMR (nuclear magnetic resonance) spectroscopy provides information on the different environments of atoms in molecules.

Learning Objectives:

- Be able to describe the use of tetramethylsilane, TMS, as the standard for chemical shift measurements.
- Be able to analyse a carbon-13 NMR spectrum of an organic molecule to make predictions about the number of carbon environments in an organic molecule, the different types of carbon environment present, from chemical shift values, and the possible structures for the molecule.
- Be able to predict a carbon-13 NMR spectrum for a given molecule.

Specification Reference 6.3.2

NMR spectroscopy and radio waves

Nuclear magnetic resonance (NMR) spectroscopy is an analytical technique that you can use to work out the structure of an organic molecule. The way that NMR works is pretty complicated, but you only need to know the basics.

A sample of a compound is placed in a strong magnetic field and exposed to a range of different frequencies of low-energy radio waves. The nuclei of certain atoms within the molecule absorb energy from the radio waves. The amount of energy that a nucleus absorbs at each frequency will depend on the environment that it's in (see below). The pattern of these absorptions gives you information about the positions of certain atoms within the molecule, and about how many atoms of that type the molecule contains. You can piece these bits of information together to work out the structure of the molecule.

The two types of NMR spectroscopy you need to know about are **carbon-13 NMR** (or **^{13}C NMR**) and high resolution proton NMR (or ^{1}H NMR). Carbon-13 NMR gives you information about the number and type of carbon environments that are in a molecule. High resolution proton NMR gives you information about the number of hydrogen atoms that are in a molecule, and the environments that they're in.

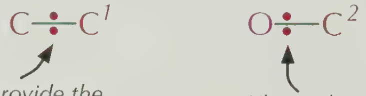
Exam Tip
You won't be asked how an NMR spectrometer works, but it'll help you to understand the spectra if you know the basics.

Nuclear environments

A nucleus is partly shielded from the effects of an external magnetic field by its surrounding electrons. Any other atoms and groups of atoms that are around a nucleus will also affect the amount of electron shielding. So the nuclei in a molecule feel different magnetic fields depending on their environments.

Example

If a carbon atom bonds to a more electronegative atom (like oxygen) the amount of electron shielding around its nucleus will decrease.



These electrons provide the carbon atoms with shielding from a magnetic field.

These electrons are pulled further away from the carbon atom by the electronegative oxygen atom. The carbon atom is less shielded.

This means that carbon 1 and carbon 2 are in different environments.

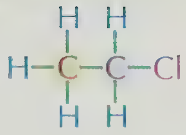
Nuclei in different environments will absorb different amounts of energy at different frequencies. It's these differences in absorption of energy between environments that you're looking for in NMR spectroscopy.

An atom's environment depends on all the groups that it's connected to, going right along the molecule — not just the atoms it's directly bonded to. To be in the same environment, two atoms must be joined to exactly the same things.

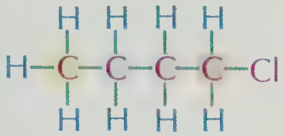
Figure 1: *An NMR spectrometer.*

Examples

Chloroethane has 2 carbon environments — its carbons are bonded to different atoms.



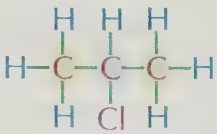
$$\begin{array}{cccc} & H & H & \\ H- & C- & C- & Cl \\ & H & H & \end{array}$$



$$\begin{array}{cccccc} & H & H & H & H & \\ H- & C- & C- & C- & C- & Cl \\ & H & H & H & H & \end{array}$$

1-chlorobutane has 4 carbon environments — the carbons are different distances from the Cl atom, so their environments are different.

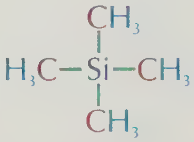
2-chloropropane has 2 carbon environments — it's symmetrical, so the carbons on each end are in the same environment.



$$\begin{array}{ccccc} & H & H & H & \\ H- & C- & C- & C- & H \\ & H & Cl & H & \end{array}$$

Chemical shift

NMR spectroscopy measures differences in the energy absorbed by nuclei in different environments relative to a standard substance — the difference is called the **chemical shift** (δ). The standard substance is tetramethylsilane (TMS).

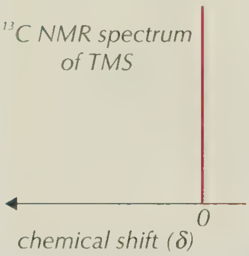


$$\begin{array}{ccc} & CH_3 & \\ H_3C- & Si & -CH_3 \\ & CH_3 & \end{array}$$

tetramethylsilane (TMS)

This molecule has 12 hydrogen atoms in identical environments and 4 carbon atoms in identical environments. This means that, in both proton NMR and ^{13}C NMR, it will produce a single absorption peak. Chemical shift is measured in parts per million (ppm) relative to TMS. So the single peak produced by TMS is given a chemical shift value of 0. You'll often see a peak at $\delta = 0$ on a spectrum. This is because TMS is added to the test compound for calibration purposes.

Tip: Here's the ^{13}C NMR spectrum for TMS:



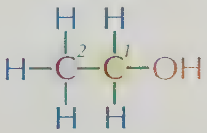
Tip: TMS is chosen as a standard because the absorption peak is at a lower frequency than just about everything else.

Interpreting ^{13}C NMR spectra

If you have a sample of a chemical that contains carbon atoms you can use a ^{13}C NMR spectrum of the molecule to help work out what it is. The spectrum gives you information about the number of carbon environments in the molecule.

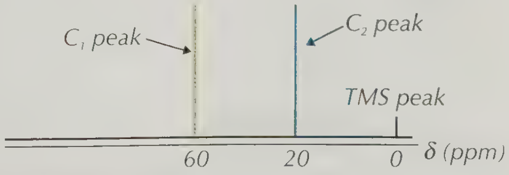
Example — **Maths Skills**

Ethanol has two carbon environments...



$$\begin{array}{cccc} & H & H & \\ H- & \overset{2}{C}- & \overset{1}{C}- & OH \\ & H & H & \end{array}$$

...and its ^{13}C NMR spectrum has two peaks.



Here are the three steps to follow to interpret a ^{13}C NMR spectrum:

1. Count the number of peaks in the spectrum (excluding the TMS peak) — this number is equal to the number of carbon environments in the molecule.
2. Use a diagram of chemical shift data to work out what kind of carbon environment is causing each peak. A diagram of typical chemical shift data for carbon-13 NMR is shown in Figure 2 on the next page.
3. Use this information to figure out the structure of the molecule.

Tip: The number of peaks of a ^{13}C spectrum doesn't necessarily equal the number of carbons in the molecule, as the molecule could have more than one carbon atom in the same environment.

Exam Tip
You'll get a diagram like this in the exam, so you don't need to learn it (phew). Just read up from any chemical shift value to find what groups could be causing a peak there.

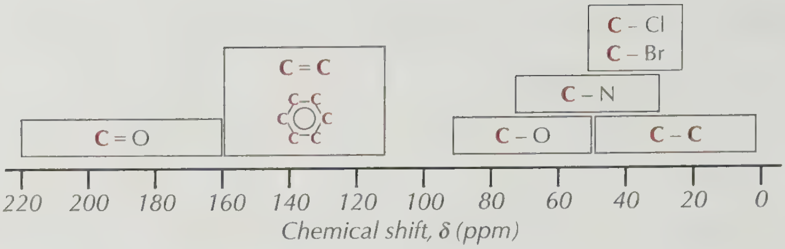
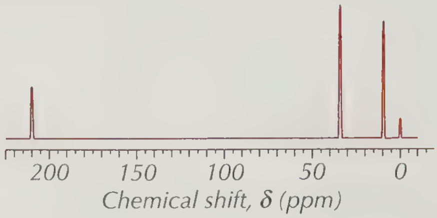


Figure 2: *Chemical shift data for carbon-13 NMR relative to TMS.*

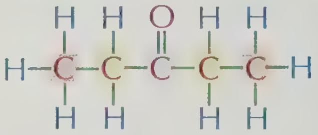
Tip: The best way to figure out the structure of a molecule is often to sketch out some possibilities. Then you can rule out any that don't have the right number of carbon environments or chemical shift values.

Example — **Maths Skills**

The carbon-13 NMR spectrum of a ketone with the molecular formula $C_5H_{10}O$ is shown below. Use the spectrum to identify the molecule.



1. The spectrum has three peaks, so the molecule must have three carbon environments.
2. The peak at $\delta = 10$ ppm represents carbon atoms in alkyl groups. We're told that the molecule is a ketone so the peak at $\delta = 35$ ppm must also be due to carbons in C–C bonds (rather than C–N, C–Cl or C–Br bonds), as ketones only contain C, H, and O atoms. The carbons causing this peak have a different chemical shift to those causing the first peak, so they must be in a slightly different environment. The peak at $\delta = 210$ ppm is due to the carbon atom in the C=O group in the ketone.
3. You know you're looking for a ketone with the formula $C_5H_{10}O$ that has three different carbon environments. The only one that fits the bill is pentan-3-one:



Tip: Don't forget that if there's a peak at $\delta = 0$ it's a TMS peak, so you can ignore it.

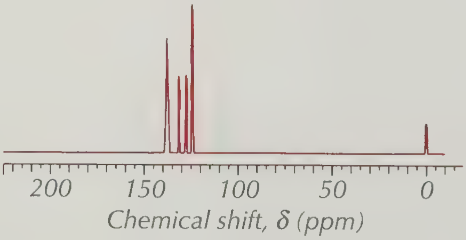
Tip: There are actually three ketones that have the formula $C_5H_{10}O$ (you could try sketching them all out) but pentan-3-one is the only one that has three carbon environments.

^{13}C NMR spectra of cyclic molecules

The number of peaks on the ^{13}C spectrum of a cyclic compound depends on the symmetry of the molecule. Here's an example to show how it works:

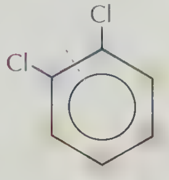
Example — **Maths Skills**

The ^{13}C NMR spectrum of an aromatic molecule with the formula $C_6H_4Cl_2$ is shown below. Identify the molecule that produced this spectrum.

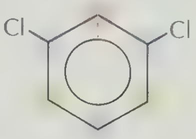


Exam Tip
Watch out for the scale on ^{13}C spectra in the exam — the chemical shift increases from right to left.

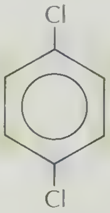
1. The spectrum has four peaks, so it must have four carbon environments.
2. All four peaks are between δ = 120 ppm and δ = 140 ppm. Looking at the chemical shift table these can only be due to alkene groups or carbons in a benzene ring. Since the question tells you that the molecule is aromatic, these carbons must be in a benzene ring.
3. There are only three aromatic molecules with the formula $C_6H_4Cl_2$ — they're all isomers of dichlorobenzene.



1,2-dichlorobenzene



1,3-dichlorobenzene



1,4-dichlorobenzene

If you look at the symmetry of the molecules you can see that 1,2-dichlorobenzene has three carbon environments, while 1,3-dichlorobenzene has four and 1,4-dichlorobenzene only has two. So the spectrum must have been produced by 1,3-dichlorobenzene.

Predicting ^{13}C NMR spectra

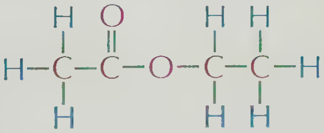
If you know the structure of a molecule, it's easy to predict what its ^{13}C NMR spectrum will look like.

Here are the steps to follow to predict a ^{13}C NMR spectrum:

1. Identify all the different carbon environments present in the molecule.
2. Look up the chemical shift values of the different environments in a chemical shift diagram.

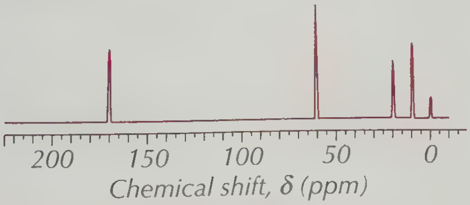
Example — Maths Skills

The molecular structure of ethyl ethanoate is shown below. Predict the number of peaks, and their corresponding shifts, on the carbon-13 NMR spectrum of ethyl ethanoate.



$$\mathrm{H-\overset{H}{\underset{H}{C}}-\overset{O}{\overset{\|}{C}}-O-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H}$$

1. There are four carbon environments — two different C–C environments, one C=O environment and one C–O environment, so there will be four peaks on the spectrum.
2. The two peaks for the C–C environments will have a shift between δ = 0 ppm and δ = 50 ppm. The peak for the C=O environment will have a shift between δ = 160 ppm and δ = 180 ppm. The peak for the C–O environment will have a shift between δ = 50 ppm and δ = 90 ppm.
3. This is what the spectrum actually looks like:



Tip: Benzene (C_6H_6) is completely symmetrical. It only has one peak on its ^{13}C NMR spectrum as all of its carbon atoms are in the same environment.

Tip: If a cyclic molecule is symmetrical, you can draw a mirror line (like the dashed lines on the molecules on the left) across it. Atoms or groups that are in the same place on opposite sides of the line will be in the same environment.

Tip: Drawing the spectrum of a molecule is really tricky — you don't know exactly where each peak will appear, or how tall each peak will be. But, you can predict how many peaks there will be, and roughly where they will appear on the spectrum.

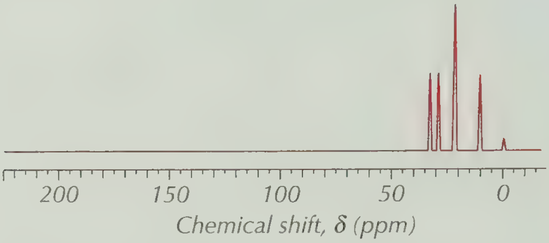
Exam Tip
It's unlikely you'll be asked to draw your prediction of a spectrum — just make sure you can work out the number of peaks and the range of shifts for each one and you'll get the marks.

Practice Questions — Application

Q1 How many peaks would you see on a ^{13}C NMR spectrum of:

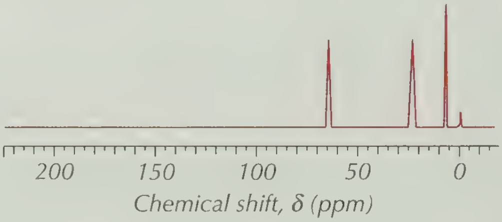
a) butanal?
b) pentane?
c) 2-methylpropane?
d) 4-chlorocyclohexanone?

Q2 The carbon-13 NMR spectrum of a compound with the molecular formula C_5H_{12} is shown below.



Use the spectrum to identify the molecule. Explain your reasoning.

Q3 The carbon-13 NMR spectrum of a molecule with the formula $C_4H_{10}O$ is shown below.

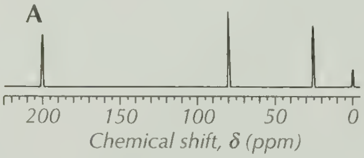


a) What type of carbon is causing the peak at $\delta = 65$?

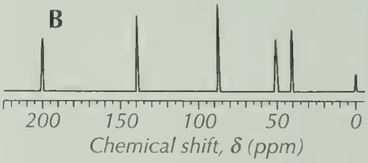
b) Use the spectrum to identify the molecule. Explain your reasoning.

Q4 Identify which of the spectra below, A, B, C or D, is the carbon-13 NMR spectrum for 3-buten-2-one.

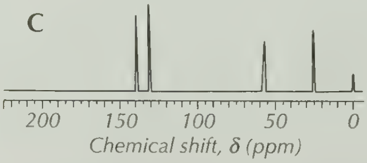
A



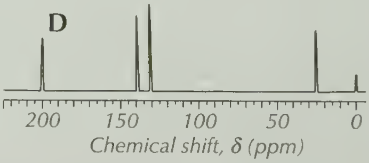
B



C



D

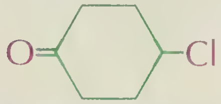


Practice Questions — Fact Recall

Q1 What is the standard substance used in NMR?

Q2 What does the number of peaks on the carbon-13 NMR spectrum of a compound correspond to?

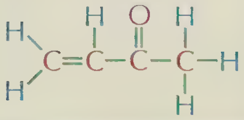
Tip: This is the structure of 4-chlorocyclohexanone:



Tip: Use the chemical shift data diagram from page 522 to help you with these questions.

Tip: Matching peaks to groups isn't always easy, because some of the chemical shift ranges overlap (e.g. a peak at $\delta = 25$ could be caused by C–C, C–Cl or C–Br). You might have to use other information that you're given — for instance if you're told that the molecule's a hydrocarbon, then it couldn't have C–Cl or C–Br in it.

Tip: The structure of 3-buten-2-one is:



Tip: Scientists use NMR spectroscopy to provide evidence that a certain compound has been synthesised.

HOW SCIENCE WORKS

5. Proton NMR Spectroscopy

This topic is all about proton NMR, also known as ^1H NMR. It works in pretty much the same way as ^{13}C NMR except this time the spectra tell you about the different hydrogen environments in a molecule.

Learning Objective:

- Be able to analyse a high resolution proton NMR spectrum of an organic molecule to make predictions about the number of proton environments in the molecule, the different types of proton environment present (from chemical shift values) and the relative numbers of each type of proton present from relative peak areas, using integration traces or ratio numbers, when required.

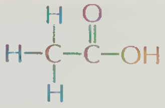
Specification Reference 6.3.2

Hydrogen environments

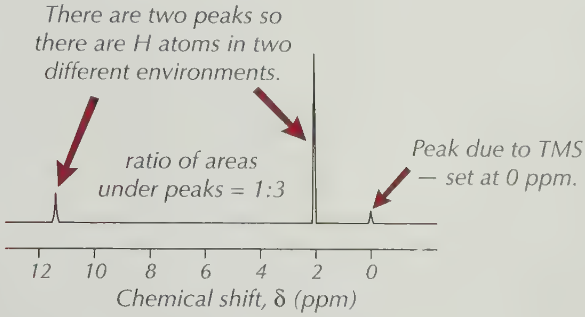
Each peak on a proton NMR spectrum is due to one or more hydrogen nuclei (protons) in a particular environment. The relative area under each peak tells you the relative number of H atoms in each environment.

Example — Maths Skills

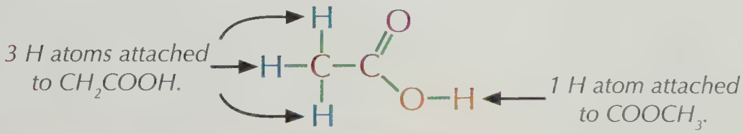
The spectrum below is the proton NMR spectrum of ethanoic acid (CH_3COOH).



ethanoic acid



There are two peaks — so there are two environments. The area ratio is 1 : 3 — so there's 1 H atom in the environment at δ = 11.5 ppm to every 3 H atoms in the other environment. If you look at the structure of ethanoic acid, this makes sense:


3 H atoms attached to CH_2COOH.
1 H atom attached to $COOCH_3$.

Tip: A relative area (or area ratio) of 1 : 3 means that the area under the second peak is three times bigger than the area under the first peak — so it must have been created by three times as many hydrogens.

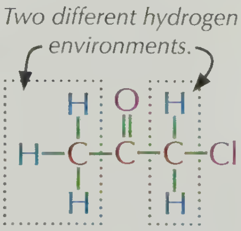
You can predict the number of peaks on a proton NMR spectrum, and the ratio of the areas under each peak, by looking at the structure of a molecule.

Example — Maths Skills

How many peaks will be present on the proton NMR spectrum of 1-chloropropanone? Predict the ratio of the areas of these peaks.

By looking at the structure of 1-chloropropanone, we can see that there are two different hydrogen environments, which means there will be 2 peaks on the proton NMR spectrum.

There are 2 hydrogens in one environment and 3 hydrogens in the other so the ratio of the peak areas will be 2 : 3.



1-chloropropanone

Exam Tip
Highlight all the hydrogens that are in the same environment the same colour — then you can go back and count up how many environments there are.

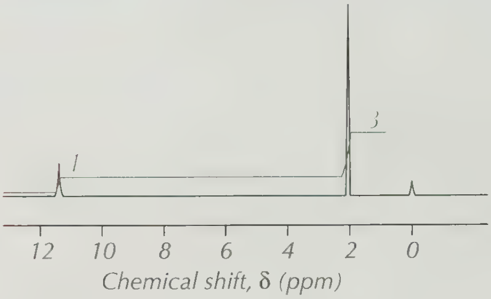
Integration traces

Proton NMR spectra can get quite cramped. Sometimes it's not easy to see the ratio of the areas — so an **integration trace** is often shown. The height increases shown on the integration trace are proportional to the areas of the peaks.

Tip: If the ratio of areas isn't given to you, you can use a ruler to measure the ratios off the integration trace. Measure the heights of the trace peaks and divide the measurements by the smallest peak height, et voilá — you've got your area ratio.

Example **Maths Skills**

Here's the spectrum for ethanoic acid again:



The integration trace (shown in green on the diagram) has a peak around 11.5 ppm and one around 2 ppm.

The heights of the vertical lines are in the ratio 1 : 3 — this means that for every one hydrogen in the first environment there are three in the second environment.

Exam Tip
Have a look at a copy of the data sheet that you'll get in the exam before the day (you can download one from OCR's website). Then you'll know exactly what's on it.

Chemical shift

You can use a diagram like the one shown in Figure 1 to identify which functional group each peak in a proton NMR spectrum is due to. Don't worry — you don't need to learn it. You'll be given one in your exam, so use it. The copy you get in your exam may look a little different, and have different values — they depend on the solvent, temperature and concentration.

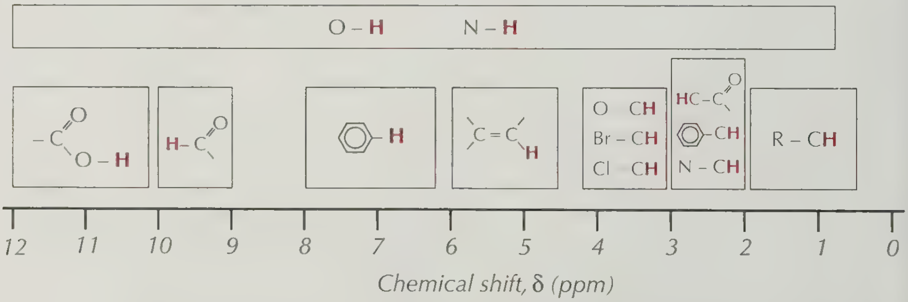
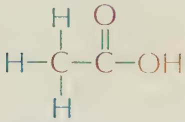


Figure 1: *Chemical shift data for proton NMR relative to TMS*

You can also use the diagram in Figure 1 to work out the different peaks on a proton NMR spectrum, from the structure of a molecule.

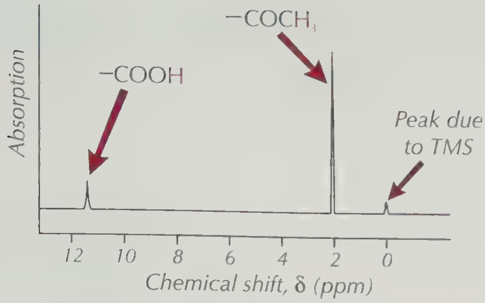
Tip: This is the structure of ethanoic acid:



Example **Maths Skills**

According to the shift diagram, ethanoic acid (CH_3COOH) should have a peak at 10 – 12 ppm due to an H atom in a -COOH group, and a peak at 2 – 3 ppm due to H atoms in a CH_3CO– group.

You can see these peaks on the proton NMR spectrum of ethanoic acid, on the next page.



Tip: Remember, if there's a peak at 0, it's just TMS and you can ignore it.

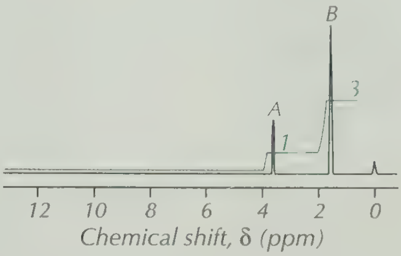
Practice Questions — Application

Q1 a) How many hydrogen environments are there in the molecule 1,2,2-tribromopropane?

b) How many peaks will the proton NMR spectrum of 1,2,2-tribromopropane have?

Q2 Draw an alkane molecule that has two hydrogen environments.

Q3 The proton NMR spectrum of a haloalkane molecule is shown on the right.



a) How many hydrogen environments are there in this molecule?

b) What is the area ratio of the peaks on this spectrum?

c) This molecule contains a total of 8 hydrogen atoms. How many hydrogen atoms are there in each environment?

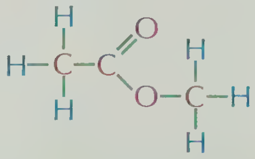
Tip: Use the chemical shift data diagram from page 526 to help you with these questions.

Q4 A scientist produces a proton NMR spectrum of a hydrocarbon. It has two peaks, one at δ = 1.7 ppm and one at δ = 4.8 ppm.

a) What is causing the peak at δ = 1.7 ppm?

b) What is causing the peak at δ = 4.8 ppm?

Q5 The ester methyl ethanoate is shown on the right.



a) How many peaks will there be on the proton NMR spectrum of methyl ethanoate?

b) What will the area ratio of the peaks on this spectrum be?

c) Predict the approximate δ values of all the peaks in this spectrum.

Figure 2: Methyl ethanoate is used as a solvent in many fast-drying spray paints and spray glues.

Practice Questions — Fact Recall

Q1 What does the number of peaks on a proton NMR spectrum tell you?

Q2 What does the area under the peaks on a proton NMR spectrum tell you?

Q3 What information would the height increases of the integration trace on a proton NMR spectrum give you?

6. More Proton NMR Spectroscopy

Time for some more about proton NMR spectra, including how NMR spectra can help you to identify molecules — plus a bit about how they're made.

Learning Objectives:

- Know how to use a high resolution proton NMR spectrum to make predictions about the number of non-equivalent protons adjacent to a given proton from the spin-spin splitting pattern, using the *n* + 1 rule.
- Understand the need for deuterated solvents, e.g. $CDCl_3$, when running an NMR spectrum.
- Know how to identify O–H and N–H protons by proton exchange using D_2O.
- Know how to use the high resolution proton NMR spectrum of a molecule to predict possible structures for the molecule.
- Be able to predict the proton NMR spectrum for a given molecule.

Specification Reference 6.3.2

Tip: You don't need to know why proton NMR peaks split. It's all down to how the tiny magnetic fields of the hydrogen nuclei interact — it's pretty tricky stuff...

Tip: Multiplets don't stop at quartets — you can go even higher. Here are some of the names for other peak splitting patterns:

5 peaks = quintet
6 peaks = sextet
7 peaks = heptet
8 peaks = octet

Splitting patterns

The peaks on a proton NMR spectrum may be split into smaller peaks (this is called spin-spin splitting). These split peaks are called **multiplets**. The splitting is caused by the influence of non-equivalent hydrogen atoms that are bonded to neighbouring carbons — these are carbons one along in the carbon chain from the carbon the hydrogen's attached to. Peaks always split into the number of non-equivalent hydrogens on the neighbouring carbons, plus one. It's called the ***n* + 1 rule**. Some of the different **splitting patterns** you'll find in proton NMR spectra are shown in Figure 1.

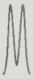
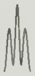
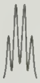
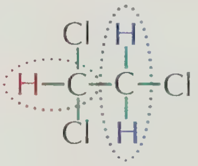
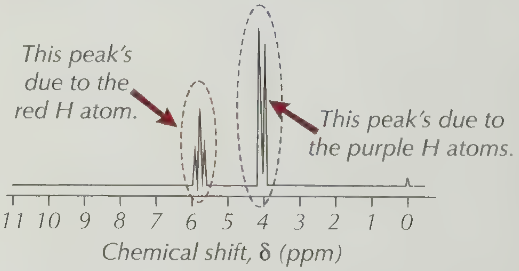
Type of peak	Structure of peak	Number of hydrogens on adjacent carbons
Singlet		0
Doublet		1
Triplet		2
Quartet		3

Figure 1: *Splitting patterns in proton NMR.*

Example — **Maths Skills**

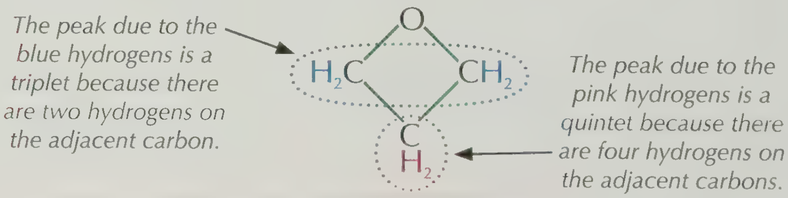
Here's the proton NMR spectrum for 1,1,2-trichloroethane:





The peak due to the purple hydrogens is split into two because there's one hydrogen on the adjacent carbon atom. The peak due to the red hydrogen is split into three because there are two hydrogens on the adjacent carbon atom.

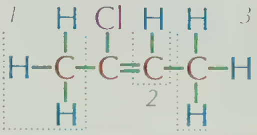
These splitting rules work just the same for cyclic (ring) compounds too. For example, look at the molecule oxetane (shown below). It has two hydrogen environments, so it has two peaks on its proton NMR spectrum:


The peak due to the blue hydrogens is a triplet because there are two hydrogens on the adjacent carbon.
O
H₂C
CH₂
C
H₂
The peak due to the pink hydrogens is a quintet because there are four hydrogens on the adjacent carbons.

Practice Questions — Application

Q1 A proton attached to carbon-1 causes a triplet on a proton NMR spectrum. How many hydrogens are on the carbon adjacent to carbon-1?

Q2 The structure of 2-chlorobut-2-ene has been drawn on the right with its hydrogen environments numbered.
For each environment, say how its peak would be split on a proton NMR spectrum of the molecule.


$H-\overset{H}{\underset{H}{C}}-\overset{Cl}{C}=\overset{H}{C}-\overset{H}{\underset{H}{C}}-H$

Tip: If you want to work out the number of hydrogens on an adjacent carbon from a peak you have to take 1 away from the number of peaks that it's split in to.

Deuterated solvents

NMR spectra are recorded with the molecule that is being analysed in solution. But if you used a ordinary solvent, like water or ethanol, the hydrogen nuclei in the solvent would add peaks to the proton NMR spectrum and confuse things.

To overcome this, the hydrogen nuclei in the solvent are replaced with deuterium (D) — an isotope of hydrogen with one proton and one neutron (see Figure 2). Deuterium nuclei don't absorb the radio wave energy, so they don't add peaks to the spectrum. A commonly used example of a '**deuterated solvent**' is deuterated chloroform, $CDCl_3$ (see Figure 3).

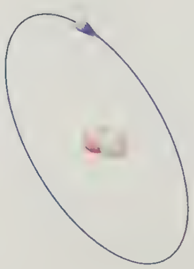


***Figure 2:** Atomic model of deuterium. Deuterium has one neutron and one proton in its nucleus, whereas hydrogen has no neutrons.*

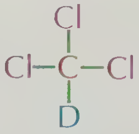


***Figure 3:** Deuterated chloroform.*

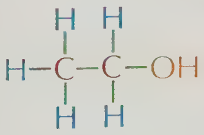
Identifying OH and NH protons

The chemical shift due to protons (H atoms) attached to oxygen (OH) or nitrogen (NH) is very variable — check out the huge ranges given in the diagram on page 526. They make a broad peak that isn't usually split (it's a singlet).

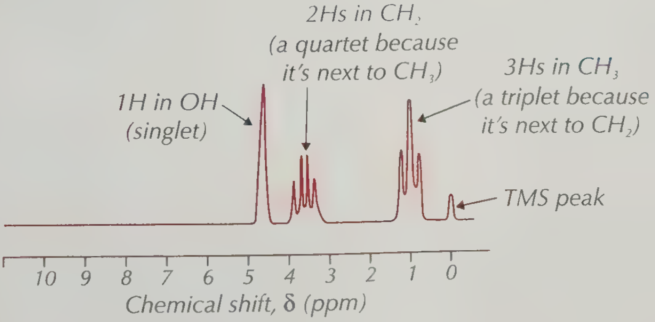
There's a clever little trick that chemists can use to identify OH and NH protons. You just run two spectra of the molecule — one with a little deuterium oxide, D_2O, added. If an OH or NH proton is present it'll swap with deuterium (to become an OD or ND group) and, hey presto, the peak that was caused by that group will disappear. (This is because deuterium doesn't absorb the radio wave energy).

Example — Maths Skills

This is the structure of ethanol:


$H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-OH$

Here's the proton NMR spectrum of ethanol:

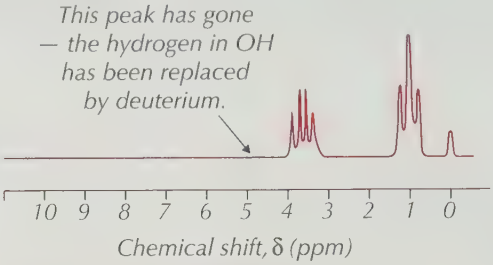


Tip: If a proton NMR spectrum has a triplet and a quartet (like the one on the left) it's very likely that the molecule that produced the spectrum will contain a CH_2CH_3 group.

Tip: Peaks caused by H atoms bonded to an O or an N (e.g. OH in alcohols or NH_2 in amines) always appear as singlets.

Tip: Remember — splitting is caused by non-equivalent protons. Take the proton NMR spectrum of ethane as an example. All the protons in ethane are equivalent, so you would get a singlet (there would be no splitting).

And here's the spectrum produced with a little D_2O added to the ethanol:



Predicting structures from proton NMR spectra

Proton NMR spectra provide you with an awful lot of information to analyse. Here's a run down of the things to look out for:

Tip: Remember, you might be given the ratio of the peak areas, or you might have to work it out from integration traces.

- The number of peaks tells you how many different hydrogen environments there are in your compound.
- You can use the chemical shift of each peak to work out what type of environment the hydrogen is in.
- The ratio of the peak areas tells you about the relative number of hydrogens in each environment.
- The splitting pattern of each peak tells you the number of hydrogens on the adjacent carbon. You can use the $n + 1$ rule to work this out.

And here's an example to help you on your way...

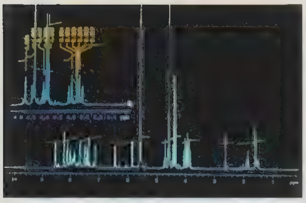
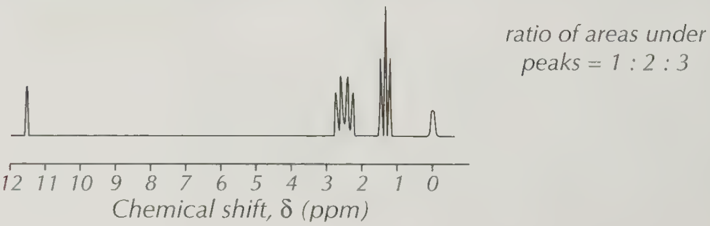


Figure 4: Proton NMR spectrum. Splitting patterns on the spectra of large organic molecules can be very complicated. Thankfully you'll never have to deal with one like this in the exam.

Example **Maths Skills**

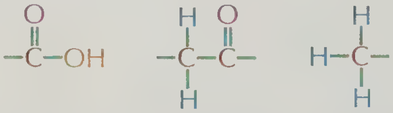
The proton NMR spectrum of a carboxylic acid is shown below. Use the spectrum and the chemical shift data on page 526 to predict its structure.



- There are three peaks so there are three different hydrogen environments.
- Using the chemical shift data, the peak at δ = 1.2 ppm should represent hydrogens in an R–CH group, the peak at δ = 2.4 ppm should represent hydrogens in a –CHCO– group, and the peak at δ = 11.5 ppm should represent a hydrogen in a –COOH group.
- From the area ratios, there's one proton in the environment at δ = 11.7 ppm for every two in the environment at δ = 2.4 ppm and every three in the environment at δ = 1.2 ppm. To fit this data the groups must be –COOH, $–CH_2CO–$ and $–CH_3$.

Exam Tip
When you're analysing a spectrum in an exam, write down all the information you're given and can work out first. Then try and work out the structure — that way you're less likely to miss out an important detail.

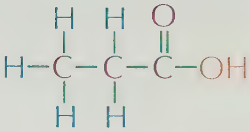
Now you know the molecule must contain these groups:



$$-\overset{\overset{\displaystyle O}{\|}}{C}-OH \qquad -\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-\overset{\overset{\displaystyle O}{\|}}{C}- \qquad H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-$$

- The peak at δ = 1.2 ppm is a triplet, so these protons must have two neighbouring hydrogens. The peak at δ = 2.4 ppm is a quartet, so these protons have three neighbouring hydrogens. The peak at δ = 11.5 ppm is a singlet, so these protons have no neighbouring hydrogens.

Now all you have to do is fit the groups together in a way that matches the splitting pattern:



$$\mathrm{H{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}\overset{O}{\overset{\|}{C}}{-}OH}$$

So this is the proton NMR spectrum of propanoic acid.

Exam Tip
Always go back and check to see if your structure matches the spectrum — you need to make sure you haven't overlooked an important piece of information.

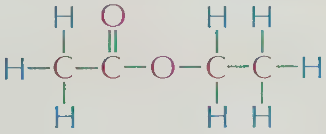
Predicting proton NMR spectra

As well as predicting the structure of a molecule from a proton NMR spectrum, you can also predict the proton NMR spectrum from the structure of a molecule. You have to think about the same things:

- How many different hydrogen environments there are in the compound tells you the number of peaks.
- The type of environment each hydrogen is in allows you to work out the chemical shift of each peak.
- The relative number of hydrogens in each environment tells you the ratio of the peak areas.
- The number of hydrogens on the adjacent carbon tells you splitting pattern of each peak.

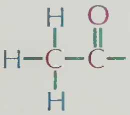
Example — **Maths Skills**

The molecular structure of ethyl ethanoate is shown below. Predict the peaks of the proton NMR spectrum of ethyl ethanoate, including the chemical shifts, area ratios and splitting patterns.

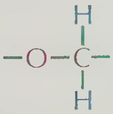


$$\mathrm{H{-}\overset{H}{\underset{H}{C}}{-}\overset{O}{\overset{\|}{C}}{-}O{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}H}$$

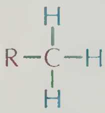
There are three different hydrogen environments, so there will be three peaks.



$$\mathrm{H{-}\overset{H}{\underset{H}{C}}{-}\overset{O}{\overset{\|}{C}}{-}}$$



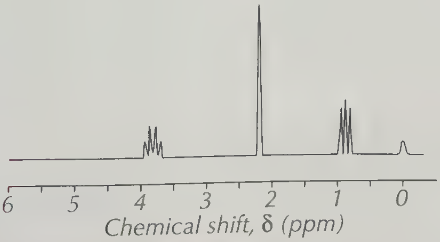
$$\mathrm{{-}O{-}\overset{H}{\underset{H}{C}}{-}}$$



$$\mathrm{R{-}\overset{H}{\underset{H}{C}}{-}H}$$

Hydrogen environment	CH_3CO-	$-OCH_2-$	$-CH_3$
Chemical shift	δ = 2-3 ppm	δ = 3-4 ppm	δ = 0.5-2 ppm
Area ratio	3	2	3
Splitting pattern	singlet as no hydrogens on neighbouring carbon	quartet due to the three hydrogens on neighbouring carbon	triplet due to the two hydrogens on neighbouring carbon

This is what the proton NMR spectrum of ethyl ethanoate actually looks like:



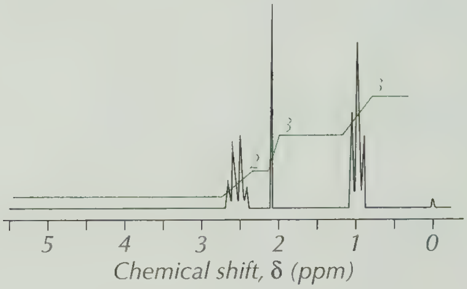
Tip: If you're asked to predict the spectrum of a particular molecule, and you're not shown its displayed structure, draw it out. This will make it so much easier to identify and work out what environment all the hydrogens are in.

Tip: Unless you're asked to specifically, don't worry about trying to draw out your prediction of a spectrum — just make sure you know how to work out how many peaks there will be, what each peak will look like and what range of shifts it will appear between.

Practice Questions — Application

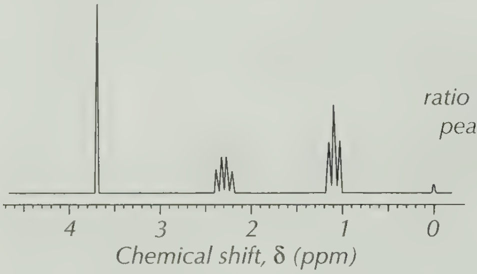
Q1 Use the proton NMR spectrum of compound **X** below, along with the chemical shift data on page 526, to work out the structure of compound **X**. HINT: Compound **X** has the molecular formula C_4H_8O.

Tip: Remember to use all the different types of information that the spectrum gives you...



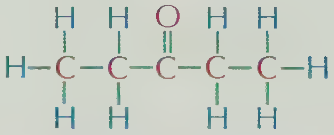
Q2 A high resolution proton NMR spectrum of an ester is shown below. Use the spectrum along with the chemical shift data on page 526, to work out the structure of the compound.

Tip: Remember esters have the functional group –COO– and are made from an alcohol and a carboxylic acid (see pages 461-462).



ratio of areas under peaks = 3 : 2 : 3

Q3 The diagram below shows the structure of pentan-3-one. Predict what pentan-3-one's proton NMR spectrum will look like in terms of the number of peaks, their position and their splitting patterns.



Exam Tip
It's really important that you use the right terms in your exam answers. Talk about peaks as doublets, triplets etc.

Practice Questions — Fact Recall

Q1 What is the *n* + 1 rule?

Q2 What's the technical name for a peak on an NMR spectrum that's been split into four smaller peaks?

Q3 Suggest one solvent that could be used to dissolve a sample for analysis by proton NMR.

Q4 You have a sample of a chemical that you think contains an OH group. Explain how you can use NMR spectroscopy to confirm that it does.

7. More on Spectra

Finally the end of the analysis section is in sight... This last topic's about how you can put together information from lots of different techniques to work out a molecule's structure.

Using elemental analysis

In elemental analysis, experiments determine the masses or percentage compositions of different elements in a compound. This data can help you to work out the empirical and molecular formulae of a compound. Look back at pages 62-65 to remind yourself how to do this. Knowing the molecular formula is useful when working out the structure of the compound from different spectra.

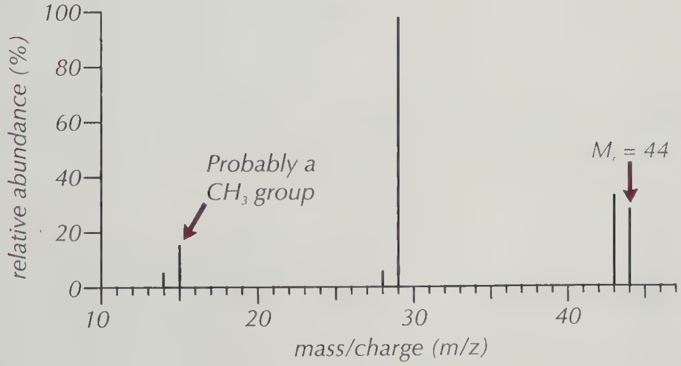
Predicting structures from spectra

All the spectroscopy techniques you've met so far will give clues to the identity of a mystery molecule, but you can be more certain about a structure (and avoid jumping to wrong conclusions) if you look at data from several different types of spectrum.

Example **Maths Skills**

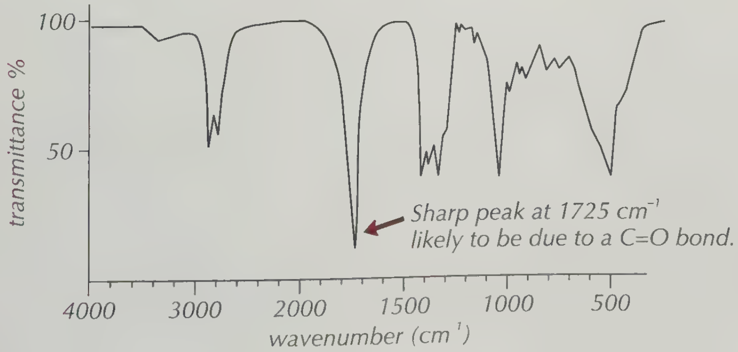
The following spectra were all obtained from the same molecule. Deduce the structure of the molecule.

Mass spectrum



This tells you that the molecule has a molecular mass of 44 and is likely to contain a CH_3 group.

Infrared spectrum



Learning Objective:

- Be able to deduce the structures of organic compounds from different analytical data, including elemental analysis, mass spectra, IR spectra and NMR spectra.

Specification Reference 6.3.2

Tip: Read over pages 267-278 for more on mass spectra and IR spectra.

Exam Tip

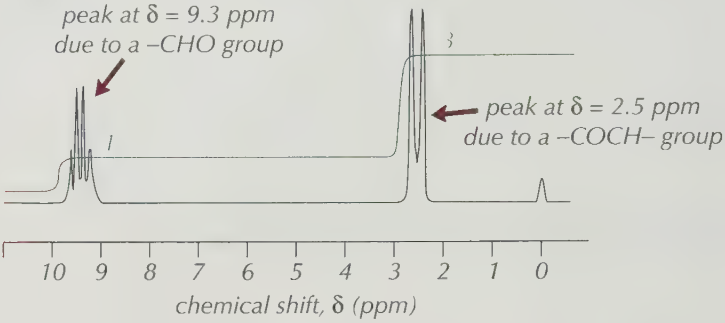
Don't forget that in the exam you'll have NMR data diagrams and infrared absorption data tables to use. There are versions of these on pages 522, 526 and 642.

***Figure 1:** Researchers using different types of spectra to identify a molecule.*

This IR spectrum strongly suggests a C=O bond in an aldehyde, ketone, ester, carboxylic acid, amide, acyl chloride or acid anhydride.

Since it doesn't also have a broad absorption between 2500 cm^{-1} and 3300 cm^{-1}, this molecule does not contain an O–H bond, so it can't be a carboxylic acid. Also, as there is no absorption between 3300 cm^{-1} and 3500 cm^{-1} there is no N–H bond either, so the molecule can't be an amide.

Proton NMR

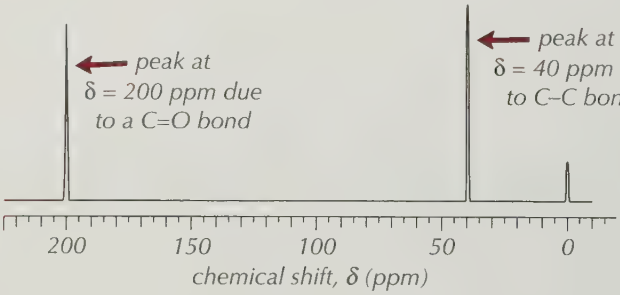


Tip: When you're solving a problem like this one, try starting off by quickly jotting down everything you can learn from each of the spectra. That way you shouldn't miss any information.

The proton NMR spectrum suggests a molecule with two hydrogen environments. The peak at δ = 9.3 ppm is due to a hydrogen in a –CHO group. (It can't be an amide group because the IR spectrum ruled that out, and it can't be a phenol group because that would give a molecule with an M_r higher than 44.) The peak at δ = 2.5 ppm is due to the hydrogen atoms in a –COCH– group. (It can't be R–NH, R–OH or HC–N because there aren't peaks matching these groups on the IR spectrum and it can't be a methylbenzene group because that would give a molecule with an M_r higher than 44.)

The area under the peaks is in the ratio 1 : 3, which means they must be –CHO and $–COCH_3$ groups. The splitting pattern shows that the protons must be on adjacent carbon atoms because they are splitting each other.

^{13}C NMR

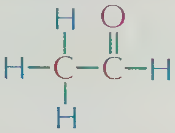


Tip: The four different types of spectra are most useful for different things. A mass spectrum gives you the M_r of the molecule. IR spectra are really handy for identifying functional groups. NMR spectra are best for working out the fine structure of the molecule once you know its formula.

The ^{13}C NMR spectrum shows that the molecule has two carbon environments. The peak at δ = 200 ppm corresponds to a carbon in a carbonyl group and the peak at δ = 40 ppm is due to an alkyl carbon. (It can't be caused by a C–N carbon because there isn't a peak matching that on the IR spectrum, and it can't be a C–Cl or C–Br carbon because that would give a molecule with an M_r higher than 44.)

Putting all this together we have a molecule with a molecular mass of 44, which contains a $–CH_3$ group next to an aldehyde group.

So the structure of the molecule must be:



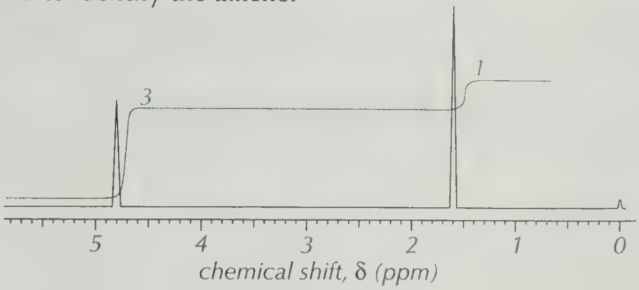
...which is the aldehyde ethanal.

Tip: When you've come up with your final answer it's a good idea to check it against all the spectra — just to make doubly sure that it fits.

You won't always get all four different kinds of spectra — sometimes you'll have to work out a structure from two or three different types of data.

Example — **Maths Skills**

An alkene with a molar mass of 56 g mol^{-1} is burnt in excess oxygen to produce 8.8 g of carbon dioxide and 3.6 g of water. The proton NMR spectrum of the alkene is shown below.
Use this data to identify the alkene.



Elemental analysis

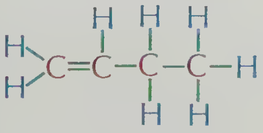
- The moles of CO_2 and H_2O produced are:

$$\text{moles } CO_2 = \frac{\text{mass}}{M_r} = \frac{8.8}{12 + (16 \times 2)} = \frac{8.8}{44} = 0.20 \text{ moles}$$

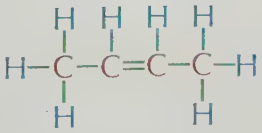
$$\text{moles } H_2O = \frac{\text{mass}}{M_r} = \frac{3.6}{(2 \times 1) + 16} = \frac{3.6}{18} = 0.20 \text{ moles}$$

- 1 mole of CO_2 contains 1 mole of carbon atoms, so you must have started with 0.20 moles of carbon atoms. 1 mole of H_2O contains 2 moles of hydrogen atoms, so you must have started with 0.40 moles (0.20 × 2) of hydrogen atoms.
- So the C : H ratio is 0.20 : 0.40, which gives a whole number C : H ratio of 1 : 2. So the empirical formula of this hydrocarbon is CH_2.
- The mass of the empirical formula is (12 × 1) + (2 × 1) = 14 g.
- Divide the molar mass of the alkene by this and you get 56 ÷ 14 = 4, so you need to scale the empirical formula up by 4 to get the molecular formula. So the molecular formula of the alkene is C_4H_8.

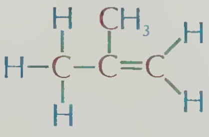
There are three alkene isomers with this molecular formula:



but-1-ene



but-2-ene



2-methylpropene

Tip: When you get to the stage where you're sure what the formula of the mystery compound is, it's a really good idea to sketch out all the isomers it could possibly be. It's usually easier to narrow down a list of options than to try drawing a molecule that fits from scratch.

Exam Tip
There's usually just one mark for identifying the molecule in a question like this. The rest come from explaining all the info you can get from the spectra — so don't worry if you can't work out exactly what it is.

Now you can use the proton NMR spectrum to work out which isomer it is.

Proton NMR

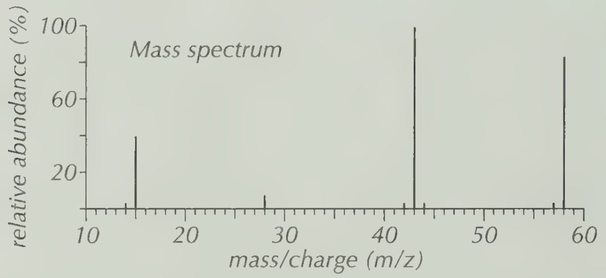
- The alkene molecule has two hydrogen environments.
- The area under the peaks is in the ratio 1 : 3.
- The peak at δ = 1.6 ppm must be due to an R–CH group (it's probably the CH_3 group). It's a singlet, so it can't be next door to any other hydrogens.
- The peak at δ = 4.8 ppm must be the H–C=C group (the alkene group). It's also a singlet, so it can't be next door to any other hydrogens either.

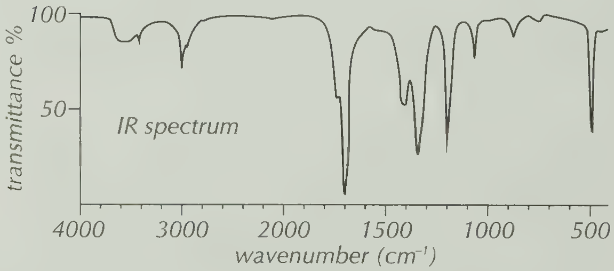
But-1-ene has four hydrogen environments, so it can't be that. But-2-ene and 2-methylpropene both have two hydrogen environments in a ratio of 1 : 3. But only 2-methylpropene has two singlets on its proton NMR spectrum. So the unknown alkene must be 2-methylpropene.

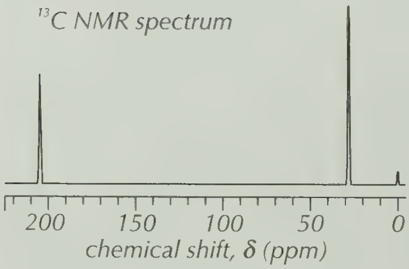
Tip: Use the tables and diagrams on pages 522, 526 and 642 to help you answer these questions.

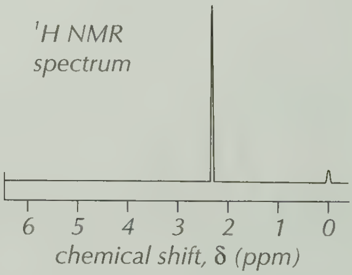
Practice Questions — Application

Q1 All four spectra shown below are for the same molecule. Use them to identify the molecule.

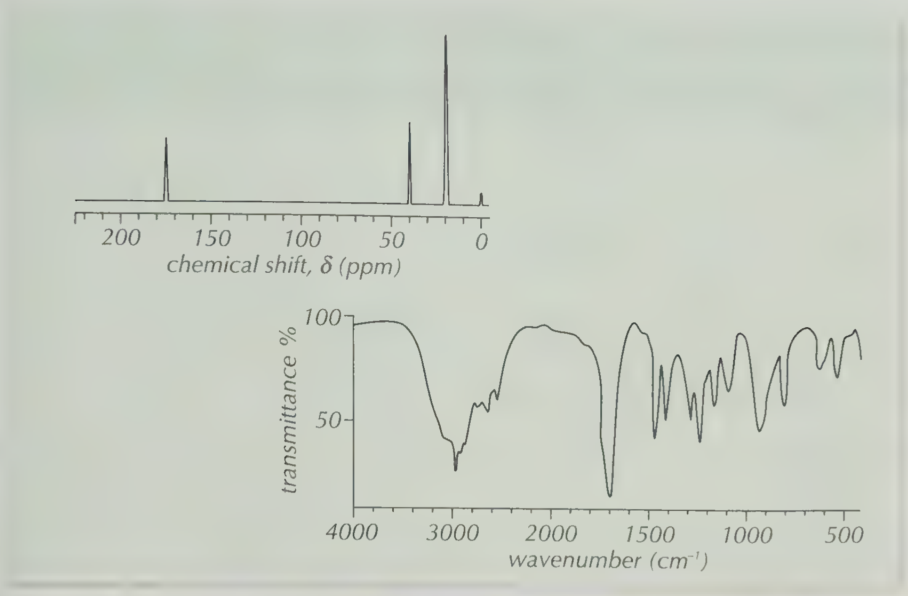








Q2 A molecule with molar mass 88 g mol^{-1} is found to have percentage composition of 55.0% carbon, 9.0% hydrogen and 36.0% oxygen by mass. The IR spectrum and the ^{13}C NMR spectrum of the molecule are shown on the next page. Use this data to identify the molecule.



Section Summary

Make sure you know...

- How to use different tests to identify organic functional groups in an unknown compound, including: bromine water as a test for alkenes, aqueous silver nitrate as a test for haloalkanes, sodium hydroxide and sodium carbonate as a test for phenols, sodium carbonate and limewater as a test for carboxylic acids, 2,4-DNP as a test for carbonyls, Tollens' reagent as a test for aldehydes and acidified potassium dichromate(VI) as a test for primary and secondary alcohols.
- How to carry out thin-layer chromatography.
- What an R_f value is and how to calculate one using a TLC chromatogram.
- How R_f values from TLC chromatograms can be used to analyse organic compounds.
- The factors that can affect the R_f values.
- How to interpret a gas chromatogram (including retention times and relative peak areas).
- The factors that affect retention times in gas chromatography.
- How to draw and use external calibration curves to estimate concentrations of components in mixtures.
- That ^{13}C NMR (carbon-13 NMR) gives you information about the number and type of carbon environments in a molecule.
- Why tetramethylsilane (TMS) is used as a standard in NMR spectroscopy.
- How to use a ^{13}C NMR spectrum to work out the structure of a molecule.
- How to predict what a ^{13}C NMR spectrum will look like for a specific molecule.
- That proton NMR (^{1}H NMR) gives you information about the number of hydrogen atoms in a molecule and the environments they're in.
- That integration traces/area ratios tell you the relative number of hydrogen atoms in different environments.
- How to use peak splitting patterns on a proton NMR spectrum to work out how many hydrogens there are on the neighbouring carbons (using the $n + 1$ rule).
- Why samples for proton NMR spectroscopy have to be dissolved in deuterated solvents, like $CDCl_3$.
- How to use deuterium oxide (D_2O) to confirm that a molecule contains a hydrogen atom in an OH or NH group using proton NMR spectroscopy.
- How to use a proton NMR spectrum to work out the structure of a molecule.
- How to predict the proton NMR spectrum for a molecule.
- How to combine data from different analytical methods to find the structure of an unknown molecule.

Exam-style Questions

1 Two chemical tests were carried out to identify an unknown organic compound, X. The results of the tests are shown in the table below.

Reaction with sodium hydroxide	**Reaction with sodium carbonate**
fizzes and forms colourless solution	nothing happens

Which of the following compounds could be X?

A CH_3NH_2

B $CH_3CH_2NH_2$

C CCl_3COOH

D C_6H_5OH

(1 mark)

2 A chemist is carrying out gas chromatography on a mixture of volatile liquids. How will increasing the temperature of the equipment affect the retention times of the components in the mixture?

A The retention times will stay the same.

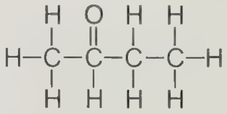
B The retention times of all of the components in the mixture will decrease.

C The retention times of all of the components in the mixture will increase

D The retention times of only the most soluble components in the mixture will decrease.

(1 mark)

3 Look at the structure of the molecule below:



Which of the following statements is **not** correct?
You can use the diagrams on pages 522 and 526 to help you with this question.

A A bright orange precipitate forms when it is reacted with 2,4–DNP.

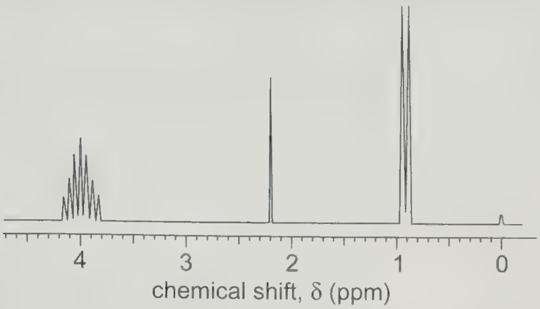
B The proton NMR spectrum has a singlet peak at δ = 2 – 3 ppm.

C A silver mirror forms when it is warmed with Tollens' reagent.

D The 13C NMR spectrum has a peak at δ = 160 – 220 ppm.

(1 mark)

4 The proton NMR spectrum of an alcohol is shown below.



(a) Suggest a solvent that you could use to dissolve the sample for this spectrum.

(1 mark)

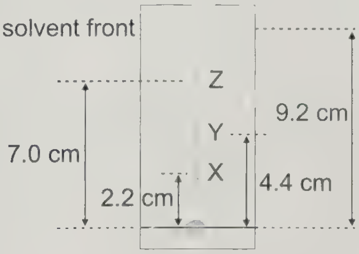
(b) Use the chemical shift values and splitting patterns to identify the chemical. Explain your reasoning. You may use the diagram on page 526 to help with this question.

(6 marks)

(c) A second proton NMR spectrum was produced for the same molecule, but this time a little D_2O was added to the sample.
Explain how this spectrum would look different to the first one.

(1 mark)

5 A scientist has a sample which contains a mixture of three different chemicals.
He uses thin-layer chromatography to separate out the components of the mixture.
The thin-layer chromatogram that he produces is shown below.



(a) Explain why the components of the mixture separate as they travel up the plate.

(2 marks)

(b) Calculate the R_f value of spot X.

(1 mark)

(c) The chemical responsible for spot Y is made up of a carbonyl with the formula C_3H_6O.
Outline a test that the scientist could carry out, on a pure sample of this chemical, to identify the structure of the carbonyl.

(3 marks)

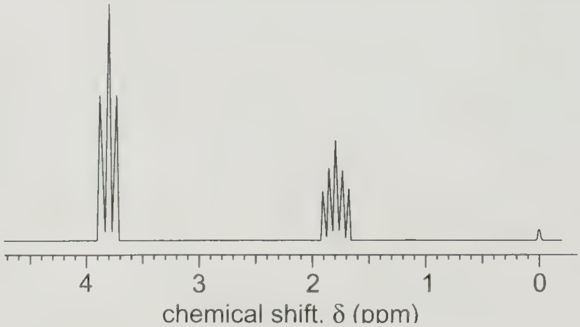
(d) The scientist reacts a pure sample of the chemical responsible for spot Z with bromine water. The solution turns from orange to colourless.
What functional group is present in the chemical responsible for spot Z?

(1 mark)

6 A student is given samples of two unknown chemicals. She is asked to use analysis techniques to identify the chemicals.

(a) The student is told that the first chemical has the molecular formula $C_3H_6Cl_2$.

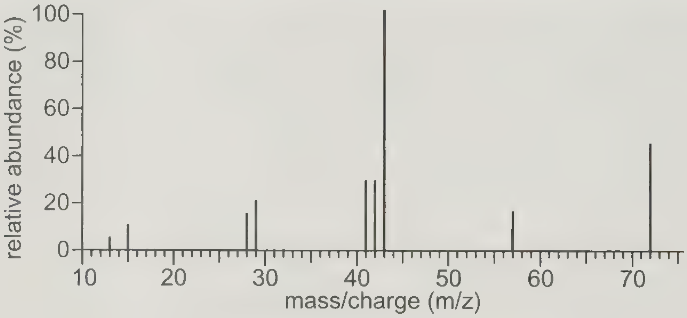
She produces a proton NMR spectrum of this chemical, which is shown below.

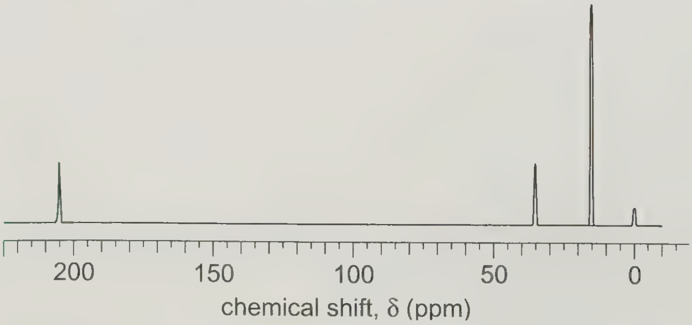


Use the chemical shift values and splitting patterns to identify the chemical.
Explain your reasoning.
You may use the diagram on page 526 to help with this question.

(6 marks)

(b) The chemical in the second sample contains only carbon, hydrogen and oxygen.
The mass spectrum and the ^{13}C NMR spectrum of this compound are shown below.





Use these spectra to identify the molecule. Explain your reasoning.
You may use the diagram on page 522 to help with this question.

(5 marks)

MATHS SKILLS

Maths Skills

Maths skills for A Level Chemistry

Maths crops up quite a lot in A Level Chemistry so it's really important that you've mastered all the maths skills you'll need before sitting your exams. Maths skills are covered throughout this book but here's an extra little section, just on maths, to help you out.

Exam Tip
Around 20% of the marks in the exams will depend on your maths skills. That's a lot of marks so it's definitely worth making sure you're up to speed.

1. Exam Technique

The way you answer calculation questions in the exams is important — you should always show your working, and remember all those pesky things like units and significant figures when giving your final answer.

Showing your working

When you're doing calculations the most important thing to remember is to show your working. You've probably heard it a million times before but it makes perfect sense. You won't get a mark for a wrong answer but you could get marks for the method you used to work out the answer.

Tip: All the examples in this book that include the kind of maths you're expected to know for your exams are clearly marked. You can spot them by the big label that says...

Maths Skills

Units

Make sure you always give the correct units for your answer (see pages 548-550 for more on units).

Example — **Maths Skills**

Here's an example of a question where you need to change the units so they match the answer the examiner wants.

1 Calculate the free energy change for the following reaction at 298 K, giving your answer in kJ mol^{-1}:

$MgCO_3 \rightarrow MgO + CO_2$ $\Delta H^\ominus = 1.17 \times 10^5$ J mol^{-1}
$\Delta S^\ominus = 175$ J K^{-1} mol^{-1}

(2 marks)

Here you use the equation: $\Delta G = \Delta H - T\Delta S$. Plugging the numbers in gives you an answer of +64 900 J mol^{-1} to three significant figures. But the question asks for the answer in kJ mol^{-1}, so you have to divide by 1000, giving an answer of 64.9 kJ mol^{-1}. If you left your answer as +64 900 J mol^{-1} you'd lose a mark.

Exam Tip
You'll need to know what units your figures need to be in for different formulas — see pages 544-546 for the units used in different formulas and pages 548-549 for how to convert between units.

Standard form

You might need to use numbers written in standard form in calculations. Standard form is used for writing very big or very small numbers in a more convenient way. Standard form must always look like this:

This number must always be between 1 and 10. → $A \times 10^n$ ← *This number is an integer and tells you the number of places and the direction in which the decimal point moves.*

Tip: '*A*' can be 1 or any number up to 10 but it can't be 10 — there can only be a single digit before the decimal point, and this digit can't be 0.

You need to be able to convert numbers written in ordinary form into standard form.

Exam Tip
If you're asked specifically to give a number in ordinary or standard form then you'll need to make sure you've written it in the correct way. If you're not told how to write a number then give it in the form that the numbers in the question are in.

Examples — Maths Skills

Here's how to write 3 500 000 in standard form.

- First write the non-zero digits with a decimal point after the first number and a '× 10' after it:

$$3.5 \times 10$$

- Then count how many places the decimal point has moved to the left. This number sits to the top right of the 10, as a superscript.

$$3\,\overset{6}{5}\,\overset{5}{0}\,\overset{4}{0}\,\overset{3}{0}\,\overset{2}{0}\,\overset{1}{0} = 3.5 \times 10^6$$

- Et voilà... that's 3 500 000 written in standard form.

Here are some more examples.

- You can write 450 000 as 4.5×10^5.
- The number 0.000056 is 5.6×10^{-5} in standard form — the *n* is negative because the decimal point has moved to the right instead of the left.
- You can write 0.003456 as 3.456×10^{-3}.

You also need to be able to convert numbers written in standard form into ordinary form.

Tip: It can be tricky to remember which way to move the decimal point. If *n* is positive then it means the number you're converting is a high number, and you'll need to move the decimal point to the right — you need more digits in front of the decimal point. If *n* is negative then you're dealing with a very low number and the decimal point needs to move to the left.

Examples — Maths Skills

Here's how to write 7.2×10^3 in ordinary form.

- Take the number in standard form, move the decimal point 3 places to the right and fill in the gaps with zeros.

$$7\,\overset{1}{2}\,\overset{2}{0}\,\overset{3}{0} = 7200$$

- There you go... that's 7.2 × 103 written in standard form.

Here are some more examples.

- You can write 9.1 × 105 as 910 000.
- The number 3.3×10^{-4} is 0.00033 in ordinary form — the n is negative so the decimal point has moved to the left instead of the right.
- You can write 1.765×10^{-3} as 0.001765.

You can do calculations with numbers that are in ordinary form and numbers that are in standard form.

Exam Tip
Make sure you know how to use standard form on your calculator — it'll make these kinds of calculations much easier.

Example — Maths Skills

How many atoms are there in 5.00 moles of carbon?

To work this out you need to use the Avogadro constant (which is written in standard form) and the equation for calculating the number of particles in an amount of substance.

The Avogadro constant = 6.02×10^{23}

no. of particles = no. moles × the Avogadro constant

So... number of atoms in 5.00 moles of carbon = $5.00 \times (6.02 \times 10^{23})$

$= 3.01 \times 10^{24}$

Significant figures

Use the number of significant figures given in the question as a guide for how many to give in the answer. You should always give your answer to the lowest number of significant figures (s.f.) given in the question — if you're really unsure, write down the full answer and then round it to 3 s.f. It always helps to write down the number of significant figures you've rounded to after your answer — it shows the examiner you haven't just made a mistake in your calculation. There's more information on how to use significant figures on page 16.

Exam Tip
It's so easy to mistype numbers into a calculator when you're under pressure in an exam. Always double check your calculations and make sure the answer looks sensible.

Examples — Maths Skills

In this question the data given to you is a good indication of how many significant figures you should give your answer to.

1 **(b)** Calculate the free energy change of a reaction carried out at 298 K, given that $\Delta H = -2.43$ kJ mol^{-1} and $\Delta S = 94.5$ J mol^{-1} K^{-1}.

(2 marks)

All the data values in the question are given to 3 s.f. so it makes sense to give your answer to 3 s.f. too. But sometimes it isn't as clear as that.

Exam Tip
You might get told in the question how many significant figures or decimal places to give your answer to. If you are, make sure that you follow the instructions — you'll lose marks if you don't.

3 **(b)** 18.5 cm^3 of a 0.65 mol dm^{-3} solution of potassium hydroxide reacts with 1.5 mol dm^{-3} sulfuric acid. Calculate the volume of sulfuric acid needed to neutralise the potassium hydroxide.

(2 marks)

There are two types of data in this question, volume data and concentration data. The volume data is given to 3 s.f. and the concentration data is given to 2 s.f. You should always give your answer to the lowest number of significant figures given — in this case that's to 2 s.f. The answer in full is 4.00833... cm^3 so the answer rounded correctly would be 4.0 cm^3 (2 s.f.).

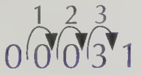
Tip: Even if the last significant figure is a zero, you still need to include it in your answer.

When you're converting between ordinary and standard form, you need to make sure the number you've converted to has the same number of significant figures as the number you've converted from. So if you've got 2 significant figures when the value is in ordinary form it also needs to be written to 2 significant figures in standard form.

Example — Maths Skills

Convert 0.00310 mol dm^{-3} from ordinary form to standard form.

- First write the non-zero digits with a decimal point after the first digit and a '× 10' after it: 3.1×10
- Then count how many places the decimal point has moved. This number needs to go as a superscript on the 10.



$= 3.1 \times 10^{-3}$

- In ordinary form, the value is given to 3 significant figures. So it needs to have 3 significant figures when it's written in standard form. So 0.00310 mol dm^{-3} is the same as:

$$3.10 \times 10^{-3} \text{ mol dm}^{-3}$$

Tip: Make sure you get the sign of the superscript correct when you're converting from ordinary form to standard form — it'll be negative for small numbers and positive for large numbers.

2. Formulas and Equations

A big part of the maths you need to do in chemistry involves using formulas and equations. So here's a nice page with them all neatly summarised for you.

Amounts of substances

First up are perhaps a couple of the most useful equations of all...

$$\text{Number of moles} = \frac{\text{Number of particles you have}}{\text{Number of particles in a mole } (N_A = 6.02 \times 10^{23})}$$

$$\text{Number of moles} = \frac{\text{Mass of substance}}{\text{Molar mass}} \qquad \text{also written as... } n = \frac{m}{M_r}$$

Tip: M_r is relative molecular mass (or relative formula mass). You work it out by adding up the A_r (atomic mass) of each atom in the compound.

You'll need these ones when you're dealing with solutions...

$$\text{Number of moles} = \frac{\text{Concentration (in mol dm}^{-3}) \times \text{Volume (in cm}^3)}{1000}$$

$$\text{Number of moles} = \text{Concentration (in mol dm}^{-3}) \times \text{Volume (in dm}^3)$$

...and these when you've got gases at room temperature and pressure.

$$\text{Number of moles} = \frac{\text{Volume (in dm}^3)}{24} \qquad \text{Number of moles} = \frac{\text{Volume (in cm}^3)}{24\,000}$$

Tip: In the formula for working out the number of moles of a gas, the "24" comes from the fact that at room temperature and pressure one mole of any gas occupies 24 dm^3. Look back at p.52 for more on this.

These two are handy when you're working out how much stuff you've made...

$$\%\text{ atom economy} = \frac{\text{Molecular mass of desired product}}{\text{Sum of molecular masses of reactants}} \times 100$$

$$\%\text{ yield} = \frac{\text{Actual yield}}{\text{Theoretical yield}} \times 100$$

Tip: The sum of the molecular masses of the reactants is the same as the sum of the molecular masses of the products.

Here's the ideal gas equation, which allows you to convert between the volume, pressure and number of moles of a gas at a given temperature:

volume (m^3) *the gas constant (= 8.314 J K^{-1} mol^{-1})*

$$pV = nRT$$

pressure (Pa) *temperature (K)*

number of moles

Exam Tip
All these formulas are really important — you have to learn them because they won't be given to you in the exam.

Reaction rates

The rate equation links the rate of a reaction to the concentration of the reactants, the orders of these reactants, and the rate constant:

rate of reaction (mol dm^{-3}s^{-1}) *reaction orders with respect to A and B (no units)*

$$\text{rate} = k[\text{A}]^m[\text{B}]^n$$

rate constant (unit varies) *concentration of reactants A and B (mol dm^{-3})*

Tip: In this equation there are only two reactants (A and B), but you can have more. Here's the equation if you have three reactants: rate = $k[\text{A}]^m[\text{B}]^n[\text{C}]^x$

You can calculate the rate constant, *k*, for a reaction using the Arrhenius equation:

pre-exponential factor (units vary)

activation energy (J mol^{-1})

$$k = Ae^{\frac{-E_a}{RT}}$$

temperature (K)

rate constant (units vary)

8.31 (J K^{-1} mol^{-1})

This rearranges into a logarithmic form:

$$\ln k = \frac{-E_a}{RT} + \ln A$$

Tip: The Arrhenius equation looks a bit beastly, but luckily you don't have to learn it — both its forms will be given to you on the data sheet.

If a reaction is first order, then the rate constant can be calculated from the half-life of the reaction, using the equation:

rate constant (s^{-1} for a first order reaction.)

$$k = \frac{\ln 2}{t_{1/2}}$$

half life (s)

pH

You need to be able to convert between pH and the concentration of H^+ ions in a solution, and vice versa:

$$pH = -\log_{10}[H^+] \qquad [H^+] = 10^{-pH}$$

You need to be able to convert between pK_a and K_a:

$$pK_a = -\log_{10} K_a \qquad K_a = 10^{-pK_a}$$

Tip: Make sure you know how to use the log button on your calculator.

Tip: You may also see '$\log_{10} x$' written as '$\log x$'.

Equilibria

You need to be able to work out equilibrium constants for reactions.

Here's the equation for the equilibrium constant (K_c).

For the general reaction $aA + bB \rightleftharpoons dD + eE$:

$$K_c = \frac{[D]^d[E]^e}{[A]^a[B]^b}$$

where [X] is the concentration of X (mol dm^{-3})

Tip: The lower-case letters a, b, d and e are the number of moles of each substance in the equation. The square brackets, [ ], mean concentration in mol dm^{-3}.

For a weak acid, the acid dissociation constant, K_a, has units of mol dm^{-3}, and is found using the formula:

$$K_a = \frac{[H^+]^2}{[HA]}$$

Water has a special dissociation constant, called the ionic product of water, K_w. The units of K_w are mol^2 dm^{-6}, and it's found using the formula:

$$K_w = [H^+][OH^-]$$

Tip: In pure water, $[H^+] = [OH^-]$ so $K_w = [H^+]^2$.

Equilibrium reactions between gases have the equilibrium constant K_p.

For the general reaction $aA + bB \rightleftharpoons dD + eE$:

$$K_p = \frac{p(D)^d p(E)^e}{p(A)^a p(B)^b}$$

where p(X) is the partial pressure of X (Pa)

You can work out the mole fractions and partial pressures of the gases in a mixture using the following equations:.

Tip: The mole fraction of a substance doesn't have any units.

$$\text{mole fraction of a gas in a mixture} = \frac{\text{number of moles of substance}}{\text{total number of moles of all substances in the mixture}}$$

$$\text{partial pressure of a gas in a mixture (Pa)} = \text{mole fraction} \times \text{total pressure of the mixture (Pa)}$$

Energy changes

Energy changes include enthalpy changes, entropy changes and free energy changes for reaction, as well as electrode potentials of electrochemical cells.

There are two formulas you need to calculate enthalpy changes of a reaction. Here's one:

Exam Tip
Make sure you can rearrange all these formulas and give the units of each quantity as well.

mass (g)

change in temperature (K or °C)

$$q = mc\Delta T$$

heat lost or gained (J)

specific heat capacity ($J\,g^{-1}\,K^{-1}$)

It doesn't matter whether the temperature is in K or °C — it's the change in temperature that goes into the formula, and that will be the same no matter what the units are.

And the slightly easier:

$$\text{Enthalpy change of reaction} = \text{Total energy absorbed} - \text{Total energy released}$$

To calculate the entropy of a system, you use:

$$\Delta S = S_{\text{products}} - S_{\text{reactants}}$$ where ΔS is the entropy change in $J\,K^{-1}\,mol^{-1}$

If you know the enthalpy change, the entropy change and temperature of a reaction, you can calculate the free energy change (ΔG) using:

Free energy change ($J\,mol^{-1}$)

Temperature (K)

$$\Delta G = \Delta H - T\Delta S$$

Enthalpy change ($J\,mol^{-1}$)

Entropy change ($J\,K^{-1}\,mol^{-1}$)

Finally, here's the equation to calculate the electrode potential of an electrochemical cell:

Tip: Electrode potentials are always measured in volts (V).

$$E^{\ominus}_{\text{cell}} = E^{\ominus}_{\text{reduced}} - E^{\ominus}_{\text{oxidised}}$$

Rearranging formulas

You'll often need to change the subject of a formula. To do this you'll need to rearrange it. The crucial thing to remember here is that whatever you do to one side of the formula you need to do exactly the same to the other side.

Example — **Maths Skills**

Use the ideal gas equation to calculate the number of moles of gas present in 1.23 m³ at a pressure of 100 000 Pa and a temperature of 298 K.

The ideal gas equation is $pV = nRT$

You need to rearrange it to make n (number of moles) the subject. To get n on its own you divide it by RT. Because you're dividing the right hand side of the equation by RT you also need to divide the left hand side by RT:

$$\frac{pV}{RT} = \frac{nRT}{RT}$$

You can cancel out RT on the right hand side...

$$\frac{pV}{RT} = \frac{n\cancel{RT}}{\cancel{RT}}$$

...which leaves you with: $\frac{pV}{RT} = n$

You can then plug in the values given in the question to work out the answer.

Tip: The subject of an equation is the component on its own on one side of the equation. So for $q = mc\Delta T$, q is the subject. For $n = \text{mass} \div M_r$, n is the subject. You'll usually want to rearrange formulas so that the thing you've been asked to calculate is the subject.

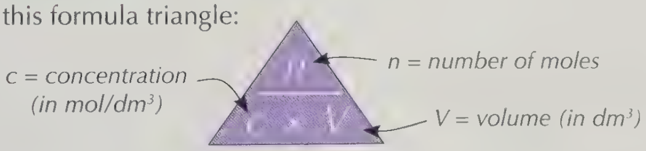
Formula triangles are really useful tools for changing the subject of an equation. If three things are related by a formula like this:

$$a = b \times c \quad \text{or like this: } b = \frac{a}{c}$$

...then you can put them into a formula triangle. The components that are multiplied together go on the bottom of the triangle. Any components that are divided go on the top. To use the formula triangle to write out a formula just cover up the component that you want to make the subject of the equation, and write down what's left.

Example — **Maths Skills**

The equation 'number of moles (n) = concentration (c) × volume (V)' can be put into this formula triangle:



If you want to make V the subject of the equation, just cover it up in the triangle and you're left with n over c, which is n divided by c. So $V = n \div c$

Tip: You don't have to use formula triangles to rearrange equations — if you're happy rearranging equations without them, then that's fine. You do need to know how to rearrange equations without a formula triangle though, as you may need to rearrange equations that don't fit nicely into a triangle. E.g. $q = mc\Delta T$

Symbols

You'll need to know the symbols which might be used in equations in the exam. You'll have seen many of these before but here's a quick refresher:

Symbol	Meaning
$<$	less than
$<<$	much less than
$>$	greater than
$>>$	much greater than

Symbol	Meaning
$=$	equal to
$\propto$	proportional to
$\sim$	approximately
$\rightleftharpoons$	reversible

3. Units

Units can trip you up if you're not sure which ones to use or how to convert between them. Here are the ones you're likely to have to deal with.

Exam Tip
You need to practise these conversions until you're sick of them. It'll save you loads of time in the exam if you're confident changing between units.

Volume

Volume can be measured in m^3, dm^3 and cm^3.

$$\begin{tikzcd} m^3 \arrow[r, bend left, "\times 1000"] & dm^3 \arrow[l, bend left, "\div 1000"] \arrow[r, bend left, "\times 1000"] & cm^3 \arrow[l, bend left, "\div 1000"] \end{tikzcd}$$

Tip: Standard form (that's showing numbers as, for example, 6×10^{-3}) is covered on pages 541 and 542.

Examples — **Maths Skills**

Write 6 dm^3 in m^3 and cm^3.

First, to convert 6 dm^3 into m^3 you need to divide by 1000.

$$6\ dm^3 \div 1000 = 0.006\ m^3 = 6 \times 10^{-3}\ m^3$$

Then, to convert 6 dm^3 into cm^3 you need to multiply by 1000.

$$6\ dm^3 \times 1000 = 6000\ cm^3 = 6 \times 10^{3}\ cm^3$$

Write 0.4 cm^3 in dm^3 and m^3.

First, to convert 0.4 cm^3 into dm^3 you need to divide by 1000.

$$0.4\ cm^3 \div 1000 = 0.0004\ dm^3 = 4 \times 10^{-4}\ dm^3$$

Then, to convert 0.0004 dm^3 into m^3 you need to divide by 1000.

$$0.0004\ dm^3 \div 1000 = 0.0000004\ m^3 = 4 \times 10^{-7}\ m^3$$

Temperature

Temperature can be measured in K and °C.

$$\begin{tikzcd} K \arrow[r, bend left, "-273"] & {^\circ C} \arrow[l, bend left, "+273"] \end{tikzcd}$$

Figure 1: A calculator. In an exam your brain can turn to mush and you can forget how to do the most simple maths. Don't be afraid to put every calculation into the calculator (even if it's just 2 × 10). If it stops you making mistakes then it's worth it.

Examples — **Maths Skills**

Write 21 °C in Kelvin.

To convert 21 °C into K you need to add 273: $21\ ^\circ C + 273 = 294\ K$

Write 298 K in °C.

To convert 298 K into °C you need to subtract 273: $298\ K - 273 = 25\ ^\circ C$

Pressure

Pressure can be measured in Pa and kPa.

$$\begin{tikzcd} kPa \arrow[r, bend left, "\times 1000"] & Pa \arrow[l, bend left, "\div 1000"] \end{tikzcd}$$

Examples — **Maths Skills**

Write 2100 Pa in kPa.

To convert 2100 Pa into kPa you need to divide by 1000:

$$2100\ Pa \div 1000 = 2.1\ kPa$$

Mass

Mass can be measured in kg and g.

$$\begin{tikzcd} \text{kg} \arrow[r, bend left, "\times 1000"] & \text{g} \arrow[l, bend left, "\div 1000"] \end{tikzcd}$$

Examples — Maths Skills

Write 4.6 kg in g.

To convert 4.6 kg into g you need to multiply by 1000.

4.6 kg × 1000 = 4600 g

Write 320 g in kg.

To convert 320 g into kg you need to divide by 1000.

320 g ÷ 1000 = 0.32 kg

Tip: If you're unsure about converting between units like these just think about a conversion you know and use that to help you. For example, if you know that 1 kg is 1000 g you know that to get from kg to g you must have to multiply by 1000 — simple.

Energy

Energy can be measured in kJ and J.

$$\begin{tikzcd} \text{kJ} \arrow[r, bend left, "\times 1000"] & \text{J} \arrow[l, bend left, "\div 1000"] \end{tikzcd}$$

Examples — Maths Skills

Write 56 kJ in J.

To convert 56 kJ into J you need to multiply by 1000.

56 kJ × 1000 = 56 000 J = 5.6×10^4 J

Write 48 000 J in kJ.

To convert 48 000 J into kJ you need to divide by 1000.

48 000 J ÷ 1000 = 48 kJ

Tip: A kJ is bigger than a J, so you'd expect the number to get smaller when you convert from J to kJ — each unit is worth more so you'll have fewer of them.

Concentration

Concentration can be measured in mol dm^{-3} and mol cm^{-3}.

$$\begin{tikzcd} \text{mol cm }^{3} \arrow[r, bend left, "\times 1000"] & \text{mol dm }^{3} \arrow[l, bend left, "\div 1000"] \end{tikzcd}$$

Examples — Maths Skills

Write 0.2 mol cm^{-3} in mol dm^{-3}.

To convert 0.2 mol cm^{-3} into mol dm^{-3} you need to multiply by 1000.

0.2 mol cm^{-3} × 1000 = 200 mol dm^{-3}

Write 34 mol dm^{-3} in mol cm^{-3}.

To convert 34 mol dm^{-3} into mol cm^{-3} you need to divide by 1000.

34 mol dm^{-3} ÷ 1000 = 0.034 mol cm^{-3}

Exam Tip

Always, always, always give units with your answer. It's really important that the examiner knows what units you're working in — 10 g is very different from 10 kg.

Life gets a bit confusing if you have to do lots of calculations one after the other — sometimes it can be difficult to keep track of your units. To avoid this, write down the units you're using with each line of the calculation. Then when you get to the end you know what units to give with your answer.

Calculating units

Some things, like the equilibrium constant (K_c) and the rate constant (k), have variable units. This means you'll need to work the units out — you can't just learn them. To work out the units, you just follow these steps:

Tip: If you have more than one of a particular unit multiplied together, you add the powers together (see p.551), e.g. (mol dm^{-3})(mol dm^{-3}) is (mol^2 dm^{-6}).

- Substitute the units that you know into the equation you're using.
- Cancel out units wherever possible — if the same unit is present on the top and the bottom of a fraction, you can cancel them out.
- Get rid of any fractions by using the index law $\frac{1}{a^n} = a^{-n}$ — any positive powers on the bottom of the fraction become negative and any negative powers become positive.

Tip: Just writing mol is the same as writing mol^1, so 1/mol = mol^{-1}.

Example — Maths Skills

The rate equation for the reaction $CH_3COCH_3 + I_2 \rightarrow CH_3COCH_2I + H^+ + I^-$ is Rate = $k[CH_3COCH_3][H^+]$. The rate of reaction is in mol dm^{-3} s^{-1} and the concentrations are in mol dm^{-3}. Find the units of k.

$$\text{Rate} = k[CH_3COCH_3][H^+] \qquad \text{so} \qquad k = \frac{\text{Rate}}{[CH_3COCH_3]\,[H^+]}$$

First substitute in the units you know:

$$\text{units of } k = \frac{\text{mol dm}^{-3}\text{s}^{-1}}{(\text{mol dm}^{-3})(\text{mol dm}^{-3})}$$

Cancel out units where you can. In this case you can cancel a mol dm^{-3} from the top and the bottom of the fraction:

$$\text{units of } k = \frac{\cancel{\text{mol dm}^{-3}}\text{s}^{-1}}{(\cancel{\text{mol dm}^{-3}})(\text{mol dm}^{-3})} = \frac{\text{s}^{-1}}{\text{mol dm}^{-3}}$$

Then get rid of the fraction by using the index law $\frac{1}{a^n} = a^{-n}$:

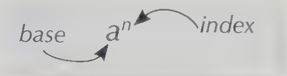
$$\text{units of } k = \text{s}^{-1}\,\text{mol}^{-1}\,\text{dm}^{3}$$

4. Indices and Logarithms

Indices and logarithms have opposite roles in maths. Indices raise a number to a power, whilst logarithms find out what a number has been raised to.

Indices

Indices are the little numbers that you raise things to the power of:



Indices can be positive or negative numbers. A positive index tells you how many times to multiply number by itself.

Examples — Maths Skills

$2^5 = 2 \times 2 \times 2 \times 2 \times 2 = \mathbf{32}$ $\qquad 10^3 = 10 \times 10 \times 10 = \mathbf{1000}$

This is how to calculate a negative index: $a^{-n} = \frac{1}{a^n}$

Tip: Indices are used a lot in rate equations. Have a look at page 303 to see them in action.

Examples — Maths Skills

$4^{-2} = \frac{1}{4 \times 4} = \mathbf{0.0625}$ $\qquad 5^{-3} = \frac{1}{5 \times 5 \times 5} = \mathbf{0.008}$

There are some rules for using indices in calculations that are useful to know:

- If you raise a number to the power 1, the answer is that number:

  $$\mathbf{a^1 = a}$$

- If you raise a number to the power 0, the answer is 1:

  $$\mathbf{a^0 = 1}$$

- If you multiply a number raised to a power by the same number raised to a different power, the answer is the same as the number raised to the sum of the two powers:

  $$\mathbf{a^n \times a^m = a^{(n+m)}}$$

- If you divide a number raised to a power by the same number raised to a different power, the answer is the same as the number raised to the value of the first power minus the value of the second power:

  $$\mathbf{a^n \div a^m = a^{(n-m)}}$$

- A number raised to a power on the bottom of a fractions is the same as that number raised to the negative of the power:

  $$\mathbf{\frac{1}{a^n} = a^{-n}}$$

Tip: These rules all apply to indices you find in units as well as in numerical equations.

Examples — Maths Skills

$7^1 = \mathbf{7}$ $\qquad 11^0 = \mathbf{1}$ $\qquad 3^2 \times 3^4 = 3^6 = \mathbf{729}$

$4^7 \div 4^5 = 4^2 = \mathbf{16}$ $\qquad \frac{1}{\text{mol dm}^{-3}} = \mathbf{mol^{-1}\ dm^3}$

The number 'e'

The number 'e' crops up occasionally in chemistry. Like 'π', it is a fixed, irrational number with an infinite number of decimal places.

$$e = 2.718281828459045235360...$$

Tip: The indices rules on the previous page all apply to calculations involving e raised to a power.

In most of the calculations involving e that you will come across, it is raised to a power. To stop you having to type in a long string of numbers every time you do these calculations, there should be a button on your calculator that looks a bit like this: e■ .

Examples **Maths Skills**

e^9 = **8103.1** e^{-4} = **0.01832** e^0 = **1**

Logarithms

Tip: Your calculator may well have buttons that look like: log■□ , log and ln . The first button lets you specify your base. The second is $\log_{10}$ and the third is $\log_e$.

Logarithms tell you how many times a number (the **base**) has been multiplied by itself to get to another number. They are the opposite of indices.

If $a^n = x$ then $\log_a x = n$

It's important to specify the base of your logarithm, but some numbers are so common they have they're own symbols:

- You often want to know how many times the number 10 has been multiplied by itself. Sometimes $\log_{10} x$ is just written as $\log x$.
- The **natural logarithm** is the logarithm with a base of e. You write $\log_e x$ as $\ln x$.

Tip: Logarithms tell you the order of magnitude a number is in, so they're really useful for comparing numbers that fall across a very large range.

These two functions are used so often that you'll probably have a button for each of them on your calculator — handy.

Examples **Maths Skills**

$\log_2 16$ = **4** $\log 100$ = **2** $\ln 14$ = **2.6**

Tip: The pH scale is a logarithmic scale in base 10. Have a look at page 341 to see more about it.

Just like for indices, there are some rules for working with logarithms in calculations that are useful to know:

- The logarithm of two things multiplied together is the same as the sum of their individual logarithms:

$$\log_a (xy) = \log_a x + \log_a y$$

- The logarithm of the value of the base raised to a power is the value of the power:

$$\log_a a^x = x$$

Tip: To make your calculations clear, always put brackets around the thing you're taking the log of. For example, log (*a* + *b*) and log(*a*) + *b* both clearly show what you're doing in a calculation. If you just write log a + b, it's not obvious what's being done.

Example **Maths Skills**

You can use these rules to rearrange the Arrhenius equation into its logarithmic form:

$$k = Ae^{\frac{-E_a}{RT}}$$

Taking the natural logarithm of both sides gives you:

$$\ln (k) = \ln (Ae^{\frac{-E_a}{RT}})$$

Using the first rule, you know that $\ln (xy) = \ln x + \ln y$, so:

$$\ln k = \ln (A) + \ln(e^{\frac{-E_a}{RT}})$$

Using the second rule, you know that $\ln e^x = x$, so:

$$\ln k = \frac{-E_a}{RT} + \ln A$$

This is the logarithmic form of the Arrhenius equation.

Tip: See pages 313-316 for lots more about the Arrhenius equation.

5. Graphs

How to construct and interpret graphs is covered on pages 17-19. But you might be asked to go a little further — for example finding an intercept or estimating a value from a graph. You'll need to understand how straight line graph equations work and how to use extrapolation and interpolation.

Straight line graphs

All straight line graphs have the general equation:

$$\underset{\text{dependent variable}}{y} = \underset{\text{gradient}}{m}\overset{\text{independent variable}}{x} + \overset{y\text{-intercept}}{c}$$

Tip: Straight line graphs you're likely to come across include rate-concentration graphs for first order reactions (page 301) and Arrhenius plots (page 315).

If you have an equation in this form and you plot a graph of the dependent variable against the independent variable, then the gradient of the graph will be equal to m, and the y-intercept will be equal to c.

Example — **Maths Skills**

The logarithmic form of the Arrhenius equation is: $\ln k = \frac{-E_a}{RT} + \ln A$

This is an equation in the form $y = mx + c$ where:

$\ln k = y$, $\frac{-E_a}{R} = m$, $\frac{1}{T} = x$, $\ln A = c$

So if you plot a graph of $\ln k$ against $\frac{1}{T}$, it will have a gradient equal to $\frac{-E_a}{R}$ and a y-intercept of $\ln A$.

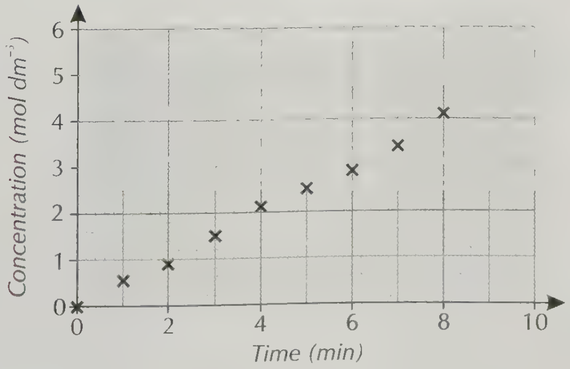
Tip: There's more about finding gradients on pages 18 and 19.

Extrapolation

Extrapolation sounds complicated but all it is is estimating a value on a graph which is outside the range of measured values.

Example — **Maths Skills**

The concentration of product A was measured over the first 8 minutes of a chemical reaction. The results are plotted on the graph below.

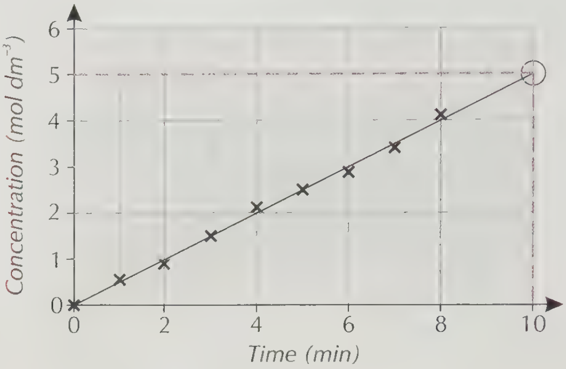


Tip: If you're having trouble remembering what extrapolation is, then remember that the original meaning of the word 'extra' is 'outside' or 'beyond'. So you're looking for an estimate 'outside' the measurements.

Tip: Remember, a line of best fit doesn't have to go through every data point. It's the line which, on average, is closest to all of the data points.

Estimate the concentration of product A at 10 minutes into the reaction.

- Draw a line of best fit through the data points on the graph.
- Continue drawing the line of best fit beyond the data points — it needs to go at least as far as the value on the *x*-axis where you've been asked to estimate a value. In this example, that's 10 minutes.
- Read off the concentration value from the line of best fit at 10 minutes.



From the line of best fit, the concentration of product A at 10 minutes would be 5 mol dm^{-3}.

Exam Tip
If you're ever having trouble drawing a line of best fit then it's a good idea to double check that you've plotted all your points correctly. If you've got any of them wrong it'll make it tricky to draw a line of best fit, and even if you do manage it it's likely to be inaccurate.

Extrapolation isn't always accurate because the graph can change between the last measurement and the point you're estimating at. In the example here, the concentration could level off somewhere between 8 and 10 minutes.

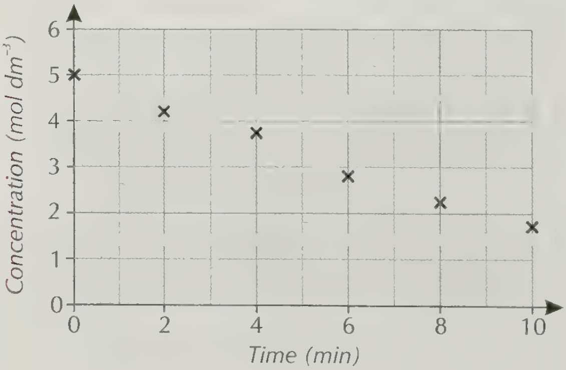
Interpolation

Interpolation is a bit like extrapolation except you're being asked to estimate a value between two points on a graph, rather than outside a range of values.

Tip: The word 'inter' means 'between'. So interpolation means making an estimation 'between' data points.

Example — Maths Skills

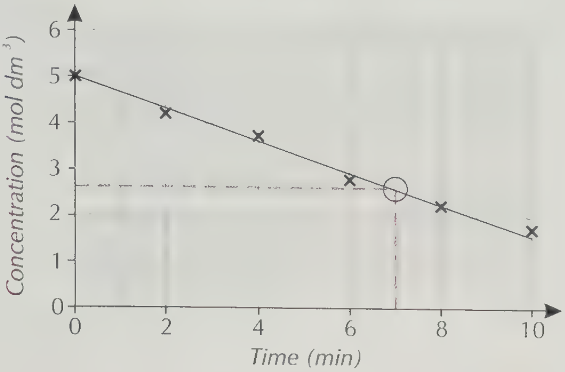
The concentration of reactant B was measured over the first 10 minutes of a chemical reaction. The results are plotted on the graph below.



Tip: Remember — not all graphs produced by experiments are nice straight lines. It could be a line which tails off, or a curve, or something completely different.

Estimate the concentration of reactant B at 7 minutes into the reaction.

- Draw a line of best fit through the data points on the graph.
- Read off the concentration value from the line of best fit at 7 minutes.



From the line of best fit, the concentration of reactant B at 7 minutes would be 2.6 mol dm^{-3}.

Exam Tip
Always use a sharp pencil for plotting points and drawing lines of best fit. If it's not sharp you'll end up with a thick line and any readings you take using it will be inaccurate.

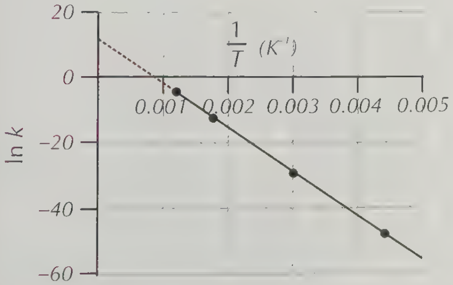
Interpolation is usually more accurate than extrapolation — this is because the line of best fit is likely to be more accurate as it just goes through measured data points. The closer together the data points are on the graph, the more accurate the results of interpolation will be.

Finding the intercept of a graph

The *y*-intercept of a graph is the point at which the line of best fit crosses the *y* axis. You may have to extrapolate your line of best fit beyond your data points to find the *y*-intercept.

Example — Maths Skills

From the logarithmic form of the Arrhenius equation, $\ln k = \frac{-E_a}{RT} + \ln A$, you know that the y-intercept of a graph of ln *k* against $\frac{1}{T}$ is equal to ln *A*.



By extrapolating the line of best fit for this graph to the point where $x = 0$, you can see that $y = 12$.

So ln *A* = **12**

Tip: You can't find the *y*-intercept from a graph if the axes have been contracted. Both axes need to run continuously from zero for it to work.

1. Exam Structure and Technique

Passing exams isn't all about revision — it really helps if you know how the exam is structured and have got your exam technique nailed so that you pick up every mark you can.

***Figure 1:** The Room of Doom awaits you. But don't panic — prepare properly and there's no reason you can't ace the exam.*

Exam Tip
Make sure you have a good read through this exam structure. It might not seem important now but you don't want to get any nasty surprises just before an exam.

Course structure

OCR A A-Level Chemistry is split into six modules, all of which are covered in this book:

Module 1 — Development of practical skills in chemistry
Module 2 — Foundations in chemistry
Module 3 — Periodic table and energy
Module 4 — Core organic chemistry
Module 5 — Physical chemistry and transition elements
Module 6 — Organic chemistry and analysis

Exam structure

For OCR A A-Level Chemistry you're gonna have to sit through three exams:

- Paper 1 — Periodic table, elements and physical chemistry
- Paper 2 — Synthesis and analytical techniques
- Paper 3 — Unified chemistry

Papers 1 and 2 are both 2 hours and 15 minutes long and are worth 100 marks each. Paper 3 is 1 hour and 30 minutes long and is worth 70 marks.

- Paper 1 covers material from Modules 1, 2, 3 and 5. It's split up into two sections. Section A has 15 marks' worth of multiple choice questions. Section B has 85 marks' worth of short and extended answer questions.
- Paper 2 covers material from Modules 1, 2, 4 and 6. It's split up into two sections. Section A has 15 marks' worth of multiple choice questions. Section B has 85 marks' worth of short and extended answer questions.
- Paper 3 covers content from all six modules. It has 70 marks' worth of short and extended answer questions.

Exam Tip
All of the exams will have a mixture of short answer and long answer questions. Short answer questions are broken down into lots of parts but they can still be worth loads of marks overall.

Level of Response questions

The exam papers include some extended response questions, where you'll usually be asked to explain or describe something at a bit more length. Some of these questions may be marked using a Level of Response mark scheme. All this means is that you'll receive marks based on the quality of your response — not just its scientific content. So the more fully explained, better structured and more coherent your answer is, the more marks you'll get.

These questions will be clearly marked on your paper, so make sure you know which ones they are and write full and well thought-out answers.

Exam Tip
Don't worry too much about Level of Response questions. Really, you should be looking to give full and coherent explanations for every extended response question.

Synoptic assessment

All the exam papers will contain some synoptic assessment. This sounds complicated but don't worry, all it means is that you could be asked to draw together and apply different bits of chemistry knowledge in the same question.

Examples

Bringing together knowledge from different parts of the course.

You might be asked how you could synthesise and purify an organic acid, and then be asked to calculate its K_a. This draws together knowledge from Modules 4, 5 and 6.

Applying knowledge from different areas to a new context.

You might be asked to draw on your knowledge of chirality to identify the stereoisomers of an organic drug molecule you've not seen before.

Time management

This is one of the most important exam skills to have. How long you spend on each question is really important in an exam — it could make all the difference to your grade. Some questions will require lots of work for only a few marks but other questions will be much quicker. Don't spend ages struggling with questions that are only worth a couple of marks — move on. You can come back to them later when you've bagged loads of other marks elsewhere.

Example

The questions below are both worth the same number of marks but require different amounts of work.

1 **(a)** Define the term 'lattice enthalpy'.

(2 marks)

2 **(a)** Use the Arrhenius plot to calculate the pre-exponential factor, *A*, of the reaction.

(2 marks)

Question 1 (a) only requires you to write down a definition — if you can remember it this shouldn't take you too long.

Question 2 (a) requires you to find the *y* intercept of a graph and then put this equal to ln *A* to calculate the pre-exponential factor — this may take you longer than writing down a definition.

So, if you're running out of time it makes sense to do questions like 1 (a) first and come back to 2 (a) if you've got time at the end.

It's worth keeping in mind that the multiple choice questions are all only worth 1 mark, even though some of them could be quite tricky and time-consuming. Don't make the mistake of spending too much time on these. If you're struggling with some of them, move on to the written answer questions where there are more marks available and then go back to the harder multiple choice questions later.

Command words

Command words are just the bit of the question that tell you what to do. You'll find answering exam questions much easier if you understand exactly what they mean, so here's a brief summary table of the most common command words:

Exam Tip

Don't stress out about synoptic assessment. You need to learn material from lots of modules for all the exams anyway, so as long as you've learnt it all thoroughly it shouldn't be a problem.

Exam Tip

Everyone has their own method of getting through the exams. Some people find it easier to go through the paper question by question and some people like to do the questions they find easiest first. The most important thing is to find out the way that suits you best before the exams — that means doing all the practice exams you can before the big day.

Exam Tip

Don't forget to go back and do any questions that you left the first time round — you don't want to miss out on marks because you forgot to do the question.

Exam Tip

Never leave a multiple choice question unanswered at the end of the exam. Even if it's a complete guess, you'll have a 25% chance of getting the mark. And if you can eliminate one or two of the options quickly, then your chances are even better.

Exam Tip
Some questions might contain more than one command word. For example, a question could start 'state and explain'. In this case, you should treat the question a little bit like two questions rolled into one. Make sure you clearly state what the question asks for and then go on to the explanation.

Command word:	What to do:
Give / Name / State	Give a brief one or two word answer, or a short sentence.
Identify	Say what something is.
Describe (an observation)	Write about what you would expect to happen in a reaction, e.g. colour change or the formation of a precipitate.
Outline / Describe (an experiment)	Write about each step in an experiment — including any equipment you would use, the reagents required and any reaction conditions (e.g. temperature, presence of a catalyst). If you are identifying a substance, you should also include any physical changes you would expect to see, such as a precipitate being formed.
Explain	Give reasons for something.
Suggest / Predict	Use your scientific knowledge to work out what the answer might be.
Calculate	Work out the solution to a mathematical problem.
Deduce / Determine	Use the information given in the question to work something out.
Compare	Give the similarities and differences between two things.
Contrast	Give the differences between two things.

Some questions will also ask you to answer 'using the information / data provided' (e.g. a graph, table, equation, etc.). When that's the case, you must use the information given and you may need to refer to it in your answer to get all the marks. Some questions may also ask you to answer 'using your calculation' — it's the same here, you need to use your answer to a particular calculation, otherwise you won't get the marks. Not all of the questions will have command words — instead they may just ask a which / what / how type of question.

Exam data sheet

When you sit your exams, you'll be given a data sheet as an insert within the exam paper. On it you'll find some useful information to help you with your exam, including...

- the molar gas volume at room temperature and pressure
- the Avogadro constant
- the specific heat capacity and the ionic product of water
- the relationship between tonnes and grams
- the gas constant
- the exponential and logarithmic forms of the Arrhenius equation
- the characteristic infrared absorptions, ^{13}C NMR shifts and ^{1}H NMR shifts of some common functional groups.

Exam Tip
It's a good idea to have a look at an exam data sheet before going in to the exam — you should be able to find it on the OCR website.

The data sheet will also contain a copy of the periodic table. You might have seen a few slightly different versions of the periodic table — for example, some tables include the lanthanides and actinides, and others don't. In the exam, make sure you use the information from the periodic table on the data sheet, even if you think it's slightly different to something you've seen elsewhere. The information on the data sheet will be what the examiners use to mark the exam papers.

2. Diagrams

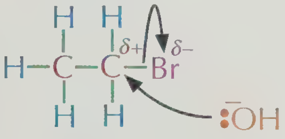
When you're asked to draw diagrams or mechanisms in an exam it's important that you draw everything correctly and include all the details that are needed.

Organic reaction mechanisms

Organic reaction mechanisms are used to show what happens during a chemical reaction. One of the most common mistakes with these is to get the curly arrows wrong.

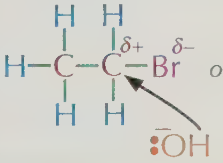
Example

When you're drawing organic reaction mechanisms the curly arrows must come from either a lone pair of electrons or from a bond, like this:

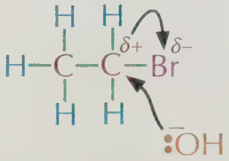


The mechanisms below are incorrect — you wouldn't get marks for them:

You won't get marks if the curly arrows come from atoms, like this...



or this...



Tip: It's important that the curly arrows come from a lone pair or a bond because that's where the electrons are found. Remember, curly arrows are supposed to show the movement of electrons.

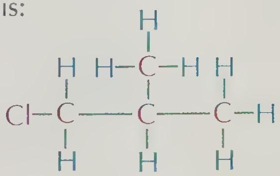
Exam Tip
Make sure that you draw carbocations with a full positive charge (+) and dipoles clearly as dipoles (δ+) — you will lose marks in the exams if it's not clear which you mean.

Displayed and skeletal formulas

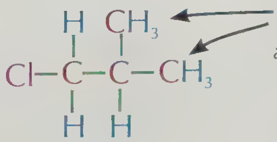
Displayed formulas show how all the atoms are connected in a molecule. It's surprisingly easy to make mistakes when drawing them.

Examples

If a question asks you for a displayed formula you have to show all of the bonds and all of the atoms in the molecule. That means you have to draw displayed formulas like this:

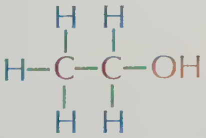


And not like this:

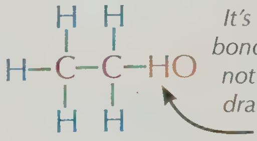


Some of the bonds between the carbon atoms and the hydrogen atoms haven't been shown, so it's not a displayed formula and you wouldn't get the marks.

If you're not asked specifically for a displayed formula then either of the diagrams above will do. Just make sure that the bonds are always drawn between the right atoms. For example, ethanol should be drawn like this:



And not like this:



It's the oxygen that's bonded to the carbon, not the hydrogen, so drawing it like this is just wrong.

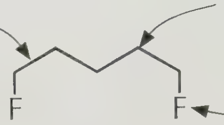
Tip: A displayed formula shows how all the atoms are arranged and all the bonds between them.

Skeletal formulas are handy when you're drawing larger organic molecules. There's a pretty good chance that you'll have to draw skeletal formulas in your exams, so you need to be able to draw them properly. Remember — bonds between carbon atoms are shown by a line and carbon atoms are found at each end. Atoms that aren't carbon or hydrogen have to be drawn on:

Exam Tip
If you're not totally comfortable drawing skeletal formulas draw out the displayed formula first and that'll help you to see what atoms need to be drawn in the skeletal formula.

Example

1,5-difluoropentane ($FCH_2CH_2CH_2CH_2CH_2F$)

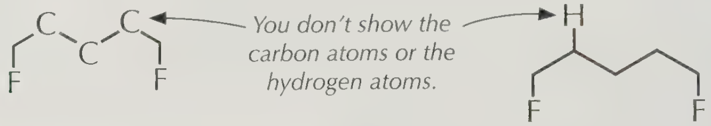


The carbon-carbon bonds are shown by lines.

Each junction represents one carbon atom.

You still have to show the atoms that aren't carbon or hydrogen.

You don't draw any carbon or hydrogen atoms from the main carbon chain when you're drawing skeletal formulas, so the diagrams below are both wrong.



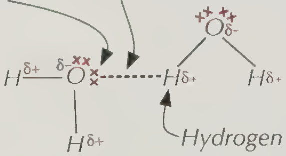
You don't show the carbon atoms or the hydrogen atoms.

Hydrogen bonds

Drawing hydrogen bonds is a common exam question. You need to know how to draw them properly to pick up all the marks you can.

Exam Tip
Make sure you've got everything the question asks for in your answer. For example, if the question asks you to include lone pairs and dipoles in a diagram, don't forget to include them.

Example



The hydrogen bond needs to come from a lone pair of electrons.

Hydrogen bond

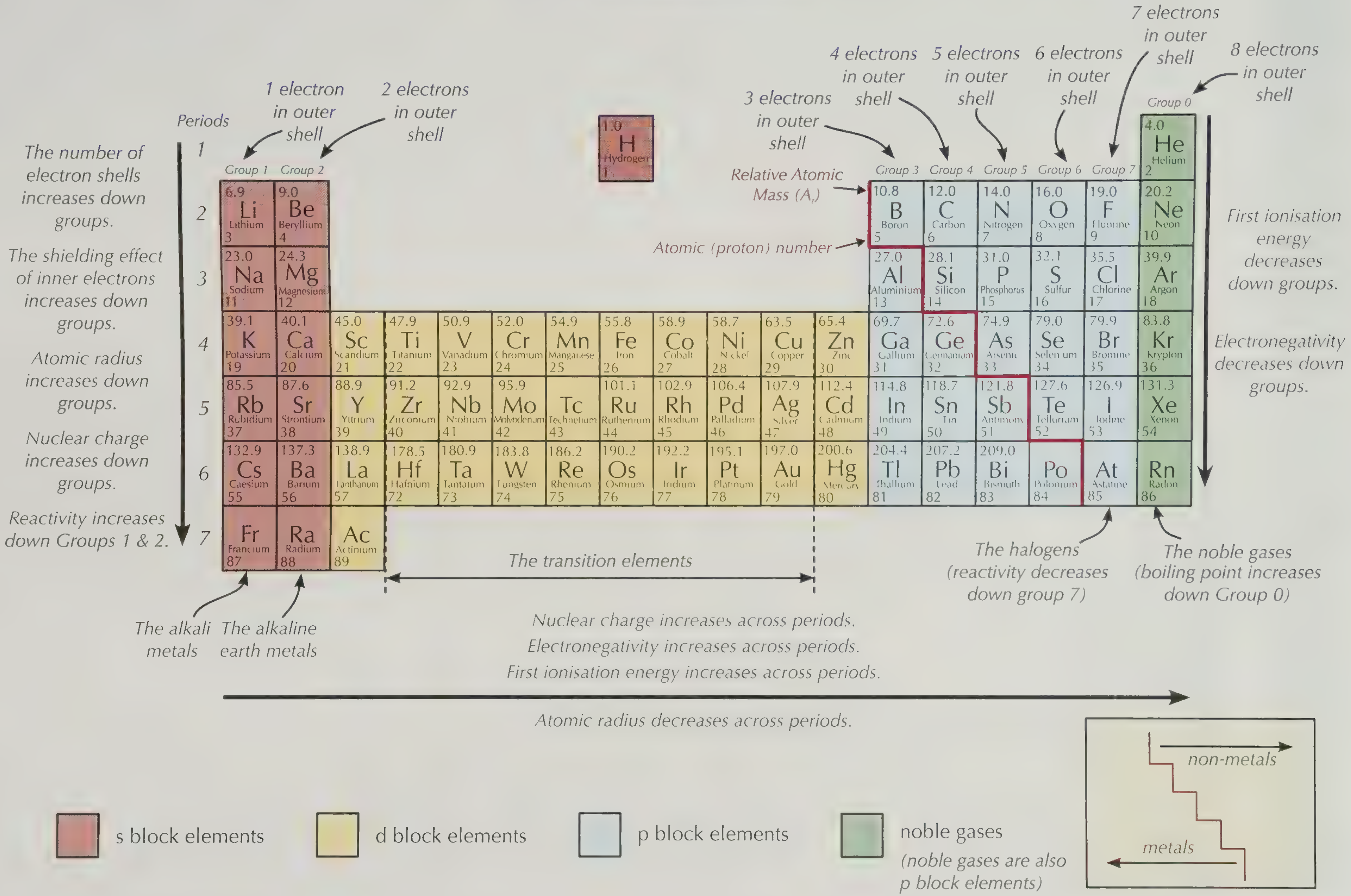
Make sure you label the hydrogen bond and put all the dipoles on the atoms.

Hydrogen bonds have to go to a hydrogen atom — duh.

General advice on diagrams

These pages cover some of the types of diagram that are likely to come up in your exams. But you could be asked to draw other diagrams. Whatever diagram you're drawing, make sure it's really clear. A small scribble in the bottom corner of a page isn't going to show enough detail to get you the marks. Draw the diagrams nice and big, but make sure that you stay within the space given for that answer. It may also help to add clear, concise labels to your diagram, particularly for things like drawings of the apparatus needed for an experiment. If you've drawn a diagram incorrectly, don't scribble part of it out and try to fix it — it'll look messy and be really hard for the examiner to figure out what you're trying to show. Cross the whole thing out and start again. And always double check that you've included all the things that you should have done.

3. The Periodic Table — Facts and Trends


Periods
1 electron in outer shell
2 electrons in outer shell
3 electrons in outer shell
4 electrons in outer shell
5 electrons in outer shell
6 electrons in outer shell
7 electrons in outer shell
8 electrons in outer shell
Relative Atomic Mass (A_r)
Atomic (proton) number
The transition elements
The alkali metals
The alkaline earth metals
non-metals
metals

The number of electron shells increases down groups.

The shielding effect of inner electrons increases down groups.

Atomic radius increases down groups.

Nuclear charge increases down groups.

Reactivity increases down Groups 1 & 2.

Periods	Group 1	Group 2											Group 3	Group 4	Group 5	Group 6	Group 7	Group 0
1								1.0 H Hydrogen 1										4.0 He Helium 2
2	6.9 Li Lithium 3	9.0 Be Beryllium 4											10.8 B Boron 5	12.0 C Carbon 6	14.0 N Nitrogen 7	16.0 O Oxygen 8	19.0 F Fluorine 9	20.2 Ne Neon 10
3	23.0 Na Sodium 11	24.3 Mg Magnesium 12											27.0 Al Aluminium 13	28.1 Si Silicon 14	31.0 P Phosphorus 15	32.1 S Sulfur 16	35.5 Cl Chlorine 17	39.9 Ar Argon 18
4	39.1 K Potassium 19	40.1 Ca Calcium 20	45.0 Sc Scandium 21	47.9 Ti Titanium 22	50.9 V Vanadium 23	52.0 Cr Chromium 24	54.9 Mn Manganese 25	55.8 Fe Iron 26	58.9 Co Cobalt 27	58.7 Ni Nickel 28	63.5 Cu Copper 29	65.4 Zn Zinc 30	69.7 Ga Gallium 31	72.6 Ge Germanium 32	74.9 As Arsenic 33	79.0 Se Selenium 34	79.9 Br Bromine 35	83.8 Kr Krypton 36
5	85.5 Rb Rubidium 37	87.6 Sr Strontium 38	88.9 Y Yttrium 39	91.2 Zr Zirconium 40	92.9 Nb Niobium 41	95.9 Mo Molybdenum 42	Tc Technetium 43	101.1 Ru Ruthenium 44	102.9 Rh Rhodium 45	106.4 Pd Palladium 46	107.9 Ag Silver 47	112.4 Cd Cadmium 48	114.8 In Indium 49	118.7 Sn Tin 50	121.8 Sb Antimony 51	127.6 Te Tellurium 52	126.9 I Iodine 53	131.3 Xe Xenon 54
6	132.9 Cs Caesium 55	137.3 Ba Barium 56	138.9 La Lanthanum 57	178.5 Hf Hafnium 72	180.9 Ta Tantalum 73	183.8 W Tungsten 74	186.2 Re Rhenium 75	190.2 Os Osmium 76	192.2 Ir Iridium 77	195.1 Pt Platinum 78	197.0 Au Gold 79	200.6 Hg Mercury 80	204.4 Tl Thallium 81	207.2 Pb Lead 82	209.0 Bi Bismuth 83	Po Polonium 84	At Astatine 85	Rn Radon 86
7	Fr Francium 87	Ra Radium 88	Ac Actinium 89															

First ionisation energy decreases down groups.

Electronegativity decreases down groups.

The halogens (reactivity decreases down group 7)

The noble gases (boiling point increases down Group 0)

Nuclear charge increases across periods.

Electronegativity increases across periods.

First ionisation energy increases across periods.

Atomic radius decreases across periods.

🟥 s block elements

🟨 d block elements

⬜ p block elements

🟩 noble gases (noble gases are also p block elements)

Answers

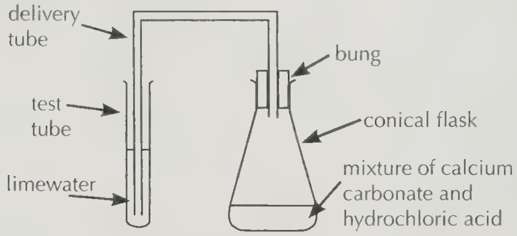
Module 1

Development of Practical Skills

1. Planning Experiments

Page 10 — Application Questions

Q1 a)



b) E.g. the chemicals used in this reaction might be harmful, so a lab coat, goggles and gloves should be used when carrying out the experiment. The hydrochloric acid should be dilute, as the more concentrated it is, the more hazardous it will be.

Q2 E.g. using test tubes means that the student won't be able to measure precisely how much gas has been given off in the experiment. He should use an appropriately sized gas syringe instead.

Q3 a) The independent variable is whether the haloalkane is a bromoalkane or a chloroalkane.

b) E.g. you could place a piece of card with an 'X' on it beneath each reaction vessel, and time how long it takes for the 'X' to disappear as the solution goes cloudy as the precipitate forms.

c) Any two from, e.g.: the temperature of the reaction / the concentration of the reactants / the volume of the reactants / the carbon skeleton of the two haloalkanes / the volume of the reaction vessel.

Page 10 — Fact Recall Questions

Q1 An independent variable is the thing you change during an experiment.

Q2 categoric

Q3 E.g. all the dangers in the experiment, who is at risk from these hazards and what you can do to reduce this risk.

2. Practical Techniques

Page 14 — Application Questions

Q1 E.g. they could put a piece of paper marked with an X under or behind the reaction vessel, and time how long it takes until they can no longer see the X.

Q2 a) A volumetric flask.

b) E.g. he could wash out the weighing vessel into the volumetric flask using the solvent used in the standard solution.

Page 14 — Fact Recall Questions

Q1 E.g. you could reweigh the weighing vessel after you transfer the solid, so you can work out the exact mass you transferred.

Q2 E.g. a pipette / a burette / a volumetric flask.

Q3 A mixture is gently heated so that the compounds evaporate off in order of increasing boiling point and can be collected separately.

3. Tables and Data

Page 16 — Application Questions

Q1 After 0 s, mean = (18.7 cm^3 + 18.4 cm^3 + 19.0 cm^3) ÷ 3
= 56.1 cm^3 ÷ 3 = **18.7 cm^3**
After 20 s, mean = (22.0 cm^3 + 21.7 cm^3 + 21.8 cm^3) ÷ 3
= 65.5 cm^3 ÷ 3 = **21.8 cm^3 (3 s.f.)**
After 40 s, mean = (24.6 cm^3 + 25.0 cm^3 + 24.8 cm^3) ÷ 3
= 74.4 cm^3 ÷ 3 = **24.8 cm^3**

Q2 First, calculate the average mass of water lost from the sample: (0.35 + 0.36 + 0.33) ÷ 3 = 0.34666...

Remember not to round your answer until right at the end.

Now use the formula moles = mass ÷ molar mass to calculate how many moles of water were lost from the sample: 0.34666... ÷ 18.0 = **0.019 mol (2 s.f.)**

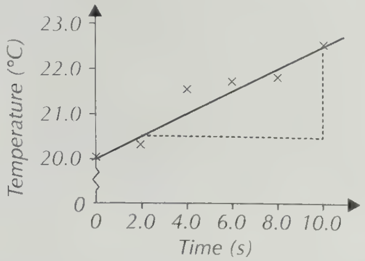
The mass changes are shown to 2 significant figures, and the molar masses are shown to 3 significant figures, so your final answer should be shown to 2 significant figures.

4. Graphs and Charts

Page 19 — Application Questions

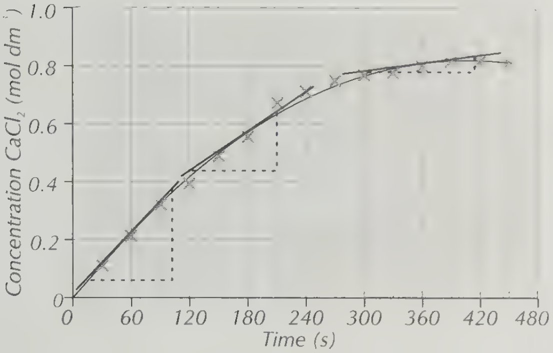
Q1 a) The result at 4 s (21.5 cm³) is anomalously high.

b)



E.g. The change in x is 8.0 s and the change in y is 2.0 °C. So the gradient is change in y ÷ change in x = 2 ÷ 8 = **0.25 °C s⁻¹**.

Q2



a) E.g. change in x = 84 s and change in y = 0.32 mol dm⁻³.

$$\text{Gradient} = \frac{\text{change in } y}{\text{change in } x} = \frac{0.32}{84}$$

= **0.0038 mol dm⁻³ s⁻¹ (2 s.f.)**

b) Change in x = 90 s and change in y = 0.22 mol dm⁻³

$$\text{Gradient} = \frac{\text{change in } y}{\text{change in } x} = \frac{0.22}{90}$$

= **0.0024 mol dm⁻³ s⁻¹ (2 s.f.)**

c) Change in x = 112 s and change in y = 0.06 mol dm⁻³.

$$\text{Gradient} = \frac{\text{change in } y}{\text{change in } x} = \frac{0.06}{112}$$

= **0.0005 mol dm⁻³ s⁻¹ (1 s.f.)**

5. Conclusions and Evaluations

Page 23 — Application Questions

Q1 a) 2.0 cm³ ÷ 2 = 1.0 cm³, so the uncertainty is **±1.0 cm³**.

b) $\text{Percentage error} = \frac{\text{uncertainty}}{\text{reading}} \times 100 = \frac{1.0}{8.0} \times 100$

= **12.5%**

c) E.g. use a measuring cylinder that has smaller increments.

Q2 a) E.g. the results will not be valid because she hasn't controlled the mass of magnesium chips. She just uses 'one spatula' which is not an accurate measurement so the mass of magnesium chips could vary between repeats. Instead, she should weigh out the same mass of magnesium to be used in each repeat.

b) She could take readings more regularly (e.g. every minute).

Exam-style Questions — pages 25-26

1 A *(1 mark)*

2 C *(1 mark)*

The result of 450 s is anomalously high so should be ignored when calculating the mean.

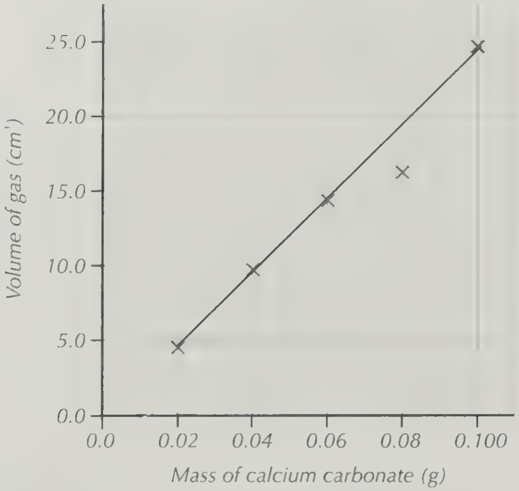
3 D *(1 mark)*

4 a) The student filled the flask until the top of the meniscus was level with the line, when he should have filled it until the bottom of the meniscus was level with the line ***(1 mark)***.

b) To make sure that all the solid has been transferred from the weighing vessel into the volumetric flask / To reduce transfer errors ***(1 mark)***.

c) To make sure the solution is mixed evenly ***(1 mark)***.

5 a)



(3 marks — 1 mark for correct, labelled axes on an appropriate scale, 1 mark for correctly plotted points, 1 mark for line of best fit ignoring anomalous point at 0.08 g.)

b) There is a positive correlation ***(1 mark)***.

c) E.g. change in x = 0.01 g, change in y = 2.5 ***(1 mark)***
gradient = 2.5 ÷ 0.01 = **250 cm³ g⁻¹** ***(1 mark)***
(allow between 210 and 290 cm³)

6 a) A separating funnel ***(1 mark)*** and a conical flask ***(1 mark)***.

b) Separating organic compounds from water soluble impurities / separating liquids of different densities ***(1 mark)***.

Module 2

Section 1 — Atoms and Moles

1. The Atom

Page 41 — Application Questions

Q1 a) 13
b) 13
c) 27 − 13 = **14**
Q2 a) 19
b) 19 + 20 = **39**
c) $^{39}_{19}\mathbf{K}$
d) 19 − 1 = **18**
Q3 a) 20 − 2 = **18**
b) 40 − 20 = **20**
Q4 a) $^{93}_{41}\mathbf{A}$ or $^{93}_{41}\mathbf{Nb}$
(mass number = 41 + 52 = 93)
b) $^{94}_{41}\mathbf{A}$ or $^{94}_{41}\mathbf{Nb}$
The atomic number must be the same, but the mass number must be different as an isotope will have a different number of neutrons.
Q5 a) A and C both have 10 electrons.
b) A and D both have 8 protons.
c) B and C both have 10 neutrons.
(17 − 7 = 10 and 20 − 10 = 10)
d) B and D both have 10 neutrons.
(17 − 7 = 10 and 18 − 8 = 10)
e) A and D are isotopes of each other because they have the same number of protons (8) but different numbers of neutrons.
(A has 16 − 8 = 8 and D has 18 − 8 = 10)

Page 41 — Fact Recall Questions

Q1 proton, neutron, electron
Q2 proton: 1, neutron: 1, electron: 1/2000
Q3 Protons and neutrons are found in the nucleus. Electrons are found in orbitals around the nucleus.
Q4 The total number of protons and neutrons in the nucleus of an atom.
Q5 The number of protons in the nucleus of an atom.
Q6 By subtracting the atomic number from the mass number.
Q7 Atoms with the same number of protons but different numbers of neutrons.
Q8 Chemical properties of an element are decided by the number and arrangement of electrons. Isotopes have the same configuration of electrons so have the same chemical properties.
Q9 Physical properties depend on the mass of an atom. Isotopes have different masses so can have different physical properties.

2. Atomic Models

Page 44 — Fact Recall Questions

Q1 Dalton described atoms as solid spheres.
J J Thomson suggested that atoms were not solid spheres — he thought they contained small negatively charged particles (electrons) in a positively charged "pudding".
Q2 the plum pudding model
Q3 Ernest Rutherford, Hans Geiger and Ernest Marsden.
Q4 If Thomson's model was correct the alpha particles fired at the sheet of gold should have been deflected very slightly by the positive "pudding" that made up most of the atom. Instead, most of the alpha particles passed straight through the gold atoms, and a very small number were deflected backwards. So the plum pudding model couldn't be right.
Q5 Rutherford's model has a tiny positively charged nucleus at the centre surrounded by a "cloud" of negative electrons. Most of the atom is empty space.
Q6 In Bohr's model the electrons only exist in fixed shells and not anywhere in between. Each shell has a fixed energy. When an electron moves between shells electromagnetic radiation is emitted or absorbed. Because the energy of the shells is fixed, the radiation will have a fixed frequency.
Q7 No

3. Relative Mass

Pages 47-48 — Application Questions

Q1 a) 85.5
b) 200.6
c) 65.4
You can just read these A_rs off the periodic table. There's one on the last page of this book.
Q2 A_r = ((0.100 × 180) + (26.5 × 182) + (14.3 × 183) + (30.7 × 184) + (28.4 × 186)) ÷ 100 = 183.891 ≈ **183.9**
Q3 Zirconium-90 (^{90}Zr), zirconium-91 (^{91}Zr), zirconium-92 (^{92}Zr), zirconium-94 (^{94}Zr) and zirconium-96 (^{96}Zr).
Q4 a) 25.0
b) 9.2
c) 9.1
d) 43.6
Q5 a) A_r = ((79 × 60.8) + (81 × 59.2)) ÷ 120 = 79.986 ≈ **80.0**
b) A_r = ((6 × 11.1) + (7 × 138.9)) ÷ 150 = 6.926 ≈ **6.9**
c) A_r = ((39 × 130.6) + (41 × 9.4)) ÷ 140 = 39.134 ≈ **39.1**
Q6 a) 14 + (3 × 1) = **17**
b) 12 + (16 × 2) = **44**
c) (12 × 2) + (1 × 4) + (16 × 6) + (14 × 2) = **152**
Q7 a) 40.1 + (35.5 × 2) = **111.1**
b) 24.3 + 32.1 + (16 × 4) = **120.4**
c) 23 + 16 + 1 = **40**

Page 48 — Fact Recall Questions

Q1 The weighted mean mass of an atom of an element compared to 1/12 of the mass of an atom of carbon-12.
Q2 The mass of an atom of an isotope of an element compared to 1/12 of the mass of an atom of carbon-12.
Q3 The average mass of a molecule compared to 1/12 of the mass of an atom of carbon-12.
Q4 The average mass of a formula unit compared to 1/12 of the mass of an atom of carbon-12.

4. The Mole

Page 51 — Application Questions

Q1 6.02×10^{23} atoms

Q2 4 moles of Na react with 1 mole of O_2 to give 2 moles of Na_2O. So 6 moles of Na must react with 1.5 moles of oxygen to give **3 moles** of Na_2O.

Q3 a) $M_r = 19 + 19 = 38$
$M =$ **38 g mol^{-1}**
b) $M_r = 40.1 + (35.5 \times 2) = 111.1$
$M =$ **111.1 g mol^{-1}**
c) $M_r = 24.3 + 32.1 + (4 \times 16) = 120.4$
$M =$ **120.4 g mol^{-1}**

Q4 $M = 23 + 14 + (16 \times 3) = 85$ g mol^{-1}
number of moles = 212.5 ÷ 85 = **2.5 moles**

Q5 $M = 65.4 + (35.5 \times 2) = 136.4$ g mol^{-1}
number of moles = 15.5 ÷ 136.4 = **0.114 moles**

Q6 $M = 23 + 35.5 = 58.5$ g mol^{-1}
Mass = 58.5 × 2 = **117 g**

Q7 $M = 24.3 + 12 + (3 \times 16) = 84.3$ g mol^{-1}
Mass = 84.3 × 0.25 = **21.1 g**

Q8 $M = 66 \div 1.5 =$ **44 g mol^{-1}**

Q9 $M = 16 + 16 = 32$ g mol^{-1}
number of moles = 82.1 ÷ 32 = 2.565... mol
number of molecules = $2.565... \times 6.02 \times 10^{23} =$ **1.54×10^{24}**

Q10 number of moles of atoms = $3.56 \times 10^{24} \div 6.02 \times 10^{23}$
= 5.913... mol
There are 6 atoms in 1 molecule of $MgSO_4$, so moles of $MgSO_4$ = 5.931... ÷ 6 = 0.985...
$M = 24.3 + 32.1 + (16 \times 4) = 120.4$ g mol^{-1}
mass = 0.985... × 120.4 = **119 g** (3 s.f.)

Page 51 — Fact Recall Questions

Q1 a) 6.02×10^{23}
b) The Avogadro constant.

Q2 The mass of one mole of the chemical.

Q3 Number of moles = mass of substance ÷ molar mass

5. Gas Volumes

Page 54 — Application Questions

Q1 Number of moles = 2.4 ÷ 24 = **0.10 moles**

Q2 Number of moles = 0.65 ÷ 24 = **0.027 moles**

Q3 Number of moles = 250 ÷ 24 000 = **0.010 moles**

Q4 Volume = 0.21 × 24 = **5.04 dm^3**

Q5 Volume = 1.1 × 24 = **26.4 dm^3**

Q6 Volume = 0.028 × 24 000 = **672 cm^3**

Q7 $n = pV \div RT$
$= (70\,000 \times 0.04) \div (8.314 \times 350) =$ **0.96 moles**

Q8 $V = nRT \div p$
$= (0.65 \times 8.314 \times 280) \div 100\,000 =$ **0.015 m^3**

Q9 0.55 dm^3 = 0.55×10^{-3} m^3 35 °C = 308 K
$n = pV \div RT$
$= (90\,000 \times (0.55 \times 10^{-3})) \div (8.314 \times 308)$
= **0.019 moles**

Q10 1200 cm^3 = 1200×10^{-6} m^3 = 1.2×10^{-3} m^3
$T = pV \div nR$
$= (110\,000 \times (1.2 \times 10^{-3})) \div (0.05 \times 8.314) = 317.5$ K
317.5 K = (317.7 – 273) °C = **44.5 °C**

Q11 75 kPa = 75 000 Pa   22 °C = 295 K
$V = nRT \div p$
$= (0.75 \times 8.314 \times 295) \div 75\,000 =$ **0.025 m^3**

Q12 80 kPa = 80 000 Pa   1.5 dm^3 = 1.5×10^{-3} m^3
$n = pV \div RT$
$= (80\,000 \times (1.5 \times 10^{-3})) \div (8.314 \times 300)$
= 0.048 moles
Molar mass = mass ÷ moles = 2.6 ÷ 0.048 = 54 g mol^{-1}
So the relative molecular mass is **54**.

Q13 44 °C = 317 K   100 kPa = 100 000 Pa
$n = pV \div RT$
$= (100\,000 \times 0.003) \div (8.314 \times 317)$
= 0.114 moles
Molar mass of neon = 20.2
mass = number of moles × molar mass
= 0.114 × 20.2 = **2.30 g**

Page 54 — Fact Recall Questions

Q1 number of moles = volume in dm^3 ÷ 24

Q2 number of moles = volume in cm^3 ÷ 24 000

Q3 $pV = nRT$
p = pressure measured in pascals (Pa)
V = volume measured in m^3
n = number of moles
$R = 8.314$ J K^{-1} mol^{-1}. R is the gas constant.
T = temperature measured in kelvin (K)

Q4 If the gas syringe is too small, the plunger may be blown out of the end of the gas syringe during the experiment/reaction. This could release toxic or flammable gases into the atmosphere, which is highly dangerous.

6. Concentration Calculations

Page 56 — Application Questions

Q1 Number of moles = (2 × 50) ÷ 1000 = **0.1 moles**

Q2 Number of moles = 0.08 × 0.5 = **0.04 moles**

Q3 Number of moles = (0.7 × 30) ÷ 1000 = **0.021 moles**

Q4 Concentration = 0.25 ÷ 0.5 = **0.5 mol dm^{-3}**

Q5 Concentration = 0.08 ÷ 0.75 = **0.11 mol dm^{-3}**

Q6 Concentration = 0.1 ÷ (36 ÷ 1000) = **2.8 mol dm^{-3}**

Dividing a volume in cm^3 by 1000 converts it to dm^3. Then you can stick it into the equation concentration = number of moles ÷ volume (dm^3).

Q7 Volume = 0.46 ÷ 1.8 = **0.26 dm^3**

Q8 Volume = 0.01 ÷ 0.55 = **0.02 dm^3**

Q9 Number of moles = concentration × volume (dm^3)
= 0.8 × (75 ÷ 1000) = 0.06
M of Na_2O = (23 × 2) + 16 = 62 g mol^{-1}
Mass = moles × molar mass = 0.06 × 62 = **3.72 g**

Q10 Number of moles = concentration × volume (dm^3)
= 0.5 × (30 ÷ 1000) = 0.015
M of $CoBr_2$ = 58.9 + (79.9 × 2) = 218.7 g mol^{-1}
Mass = number of moles × molar mass
= 0.015 × 218.7 = **3.3 g**

Q11 Number of moles = concentration × volume (dm^3)
= 1.2 × (100 ÷ 1000) = 0.12
molar mass = mass ÷ number of moles
= 4.08 ÷ 0.12 = **34 g mol^{-1}**

Q12 Number of moles = concentration × volume (dm^3)
= 4.1 × (50 ÷ 1000) = 0.205
M of sodium chloride (NaCl) = 23 + 35.5 = 58.5
mass = molar mass × number of moles
= 58.5 × 0.205 = **12.0 g**

Page 56 — Fact Recall Questions

Q1 $$\text{Number of moles} = \frac{\text{concentration} \times \text{volume (in cm}^3)}{1000}$$
Number of moles = concentration × volume (dm^3)

Q2 1000

Exam-style Questions — pages 58–59

1 B ***(1 mark)***

2 C ***(1 mark)***

3 B ***(1 mark)***

4 a) Her readings would be lower than expected ***(1 mark)***.
b) E.g. Do the reaction in a fume cupboard ***(1 mark)***.
c) If the student underestimates the volume of gas in the experiment, she may select a gas syringe that is too small. The plunger may be blown out of the end of the syringe, allowing the gas to escape into the atmosphere ***(1 mark)***.

5 a) (i) Isotopes are atoms of the same element which have the same number of protons / same atomic number ***(1 mark)*** but different numbers of neutrons / different mass numbers ***(1 mark)***.
(ii)

	Protons	Neutrons	Electrons
^{28}Si	14	14	14
^{29}Si	14	15	14
^{30}Si	14	16	14

(1 mark for protons and electrons correct, 1 mark for all neutrons correct).

b) (i) The weighted mean mass of an atom of an element ***(1 mark)*** compared to 1/12 of the mass of an atom of carbon-12 ***(1 mark)***.

Make sure you talk about atoms here and not just elements or isotopes. If you say 'the mean mass of an element' or 'the mean mass of an isotope' you won't get the marks.

(ii) A_r = [(28 × 92.23) + (29 × 4.67) + (30 × 3.10)] ÷ 100 ***(1 mark)*** = 28.11 ***(1 mark)***

c) A_r = [(46 × 17.4) + (47 × 15.5) + (48 × 154.8) + (49 × 11.3) + (50 × 10.9)] ÷ (17.4 + 15.5 + 154.8 + 11.3 + 10.9) = **47.9** ***(1 mark)***
The element is titanium ***(1 mark)***.

6 a) $n = pV \div RT$
T = 58.8 + 273 = 331.8 K
n = [(178 × 10^3) × (7.89 × 10^{-3})] ÷ (8.314 × 331.8)
= 0.509... moles ***(1 mark)***
M_r = mass ÷ moles
= 22.4 ÷ 0.509... = **44.0** (3 s.f.) ***(1 mark)***

b) 44 – (16 × 2) = 12 ***(1 mark)***
12 corresponds to a single atom of carbon. Therefore the gas is carbon dioxide ***(1 mark)***.

c) At r.t.p., volume in dm^3 = moles × 24.
From part (a), moles of CO_2 = 0.509... mol.
volume in dm^3 = 0.509... × 24 = **12.2 dm^3** (3 s.f.) ***(1 mark)***

Section 2 — Formulas and Equations

1. Formulas

Page 61 — Application Questions

Q1 CH

Q2 Molecular formula: $C_2H_6O_4$, empirical formula: CH_3O_2.

Q3 a) $C_4H_8Br_2$

b) C_2H_4Br

Q4 empirical mass = (4 × 12) + (9 × 1) = 57

molecular mass = 114, so there are

(114 ÷ 57) = 2 empirical units in the molecule.

molecular formula = $\mathbf{C_8H_{18}}$

Q5 empirical mass = (3 × 12) + (5 × 1) + (2 × 16) = 73

M_r = 146, so there are (146 ÷ 73) = 2 empirical units in the molecule.

molecular formula = $\mathbf{C_6H_{10}O_4}$

Q6 empirical mass = (4 × 12) + (6 × 1) + (2 × 35.5) + (1 × 16) = 141

M_r = 423, so there are (423 ÷ 141) = 3 empirical units in the molecule.

molecular formula = $\mathbf{C_{12}H_{18}Cl_6O_3}$

Page 61 — Fact Recall Questions

Q1 The empirical formula gives the smallest whole number ratio of atoms of each element in a compound.

Q2 The molecular formula gives the actual numbers of atoms of each type of element in a molecule.

2. Calculating Formulas

Page 63 — Application Questions

Q1 moles CO_2 = mass ÷ M_r = 17.6 ÷ 44 = 0.40 mol

moles H_2O = mass ÷ M_r = 10.8 ÷ 18 = 0.60 mol

There is 1 mole of C in 1 mole of CO_2 so you must have started with 0.40 moles of C.

There are 2 moles of H in 1 mole of H_2O so you must have started with 2 × 0.60 = 1.2 moles of H.

So, the ratio of C : H = 0.40 : 1.2 = 1 : 3 and the empirical formula is $\mathbf{CH_3}$.

Q2 moles CO_2 = mass ÷ M_r = 3.52 ÷ 44 = 0.080 mol

moles H_2O = mass ÷ M_r = 2.88 ÷ 18 = 0.16 mol

There is 1 mole of C in 1 mole of CO_2 so you must have started with 0.080 moles of C.

There are 2 moles of H in 1 mole of H_2O so you must have started with 2 × 0.16 = 0.32 moles of H.

So, the ratio of C : H = 0.080 : 0.32 = 1 : 4 and the empirical formula is $\mathbf{CH_4}$.

Q3 If 5.52 g of sodium burns to give 7.44 g of sodium oxide then 7.44 – 5.52 = 1.92 g of oxygen must be added.

moles Na = mass ÷ M_r = 5.52 ÷ 23 = 0.24 mol

moles O = mass ÷ M_r = 1.92 ÷ 16 = 0.12 mol

So, the ratio of Na : O = 0.24 : 0.12 = 2 : 1 and the empirical formula is $\mathbf{Na_2O}$.

Q4 If 50.2 g of iron burns to give 69.4 g or iron oxide then 69.4 – 50.2 = 19.2 g of oxygen must be added.

moles Fe = mass ÷ M_r = 50.2 ÷ 55.8 = 0.90 mol

moles O = mass ÷ M_r = 19.2 ÷ 16 = 1.2 mol

So, the ratio of Fe : O = 0.90 : 1.2 = 3 : 4 and the empirical formula is $\mathbf{Fe_3O_4}$.

In this question the highest number of moles isn't divisible by the lowest number of moles. So to get the whole number ratio you have to divide by a common factor — in this case 0.3.

Page 64 — Application Questions

Q1 Mass of each element:

H = 5.9 g O = 94.1 g

Moles of each element:

H = (5.9 ÷ 1) = 5.9 moles

O = (94.1 ÷ 16) = 5.9 moles

Divide each by 5.9:

H = (5.9 ÷ 5.9) = 1 O = (5.9 ÷ 5.9) = 1

The ratio of H : O is 1 : 1.

So the empirical formula is **HO**.

Q2 Mass of each element:

Al = 20.2 g Cl = 79.8 g

Moles of each element:

Al = (20.2 ÷ 27) = 0.748 moles

Cl = (79.8 ÷ 35.5) = 2.248 moles

Divide each by 0.748:

Al = (0.748 ÷ 0.748) = 1 Cl = (2.248 ÷ 0.748) = 3

The ratio of Al : Cl is 1 : 3.

So the empirical formula is $\mathbf{AlCl_3}$.

Q3 Mass of each element:

C = 8.50 g H = 1.40 g I = 90.1 g

Moles of each element:

C = (8.50 ÷ 12) = 0.708 moles

H = (1.40 ÷ 1) = 1.40 moles

I = (90.1 ÷ 126.9) = 0.710 moles

Divide each by 0.708:

C = (0.708 ÷ 0.708) = 1

H = (1.40 ÷ 0.708) = 2

I = (0.710 ÷ 0.708) = 1

The ratio of C : H : I is 1 : 2 : 1.

So the empirical formula is $\mathbf{CH_2I}$.

Q4 % V = 32.3 % Cl = 100 – 32.3 = 67.7

Mass of each element:

V = 32.3 g Cl = 67.7 g

Moles of each element:

V = (32.3 ÷ 50.9) = 0.635 moles

Cl = (67.7 ÷ 35.5) = 1.91 moles

Divide each by 0.635:

V = (0.635 ÷ 0.635) = 1 Cl = (1.91 ÷ 0.635) = 3

The ratio of V : Cl is 1 : 3.

So the empirical formula is $\mathbf{VCl_3}$.

Q5 % O = 31.58 % Cr = 100 – 31.58 = 68.42

Mass of each element:

O = 31.58 g Cr = 68.42 g

Moles of each element:

O = (31.58 ÷ 16) = 1.974 moles

Cr = (68.42 ÷ 52) = 1.316 moles

Divide each by 1.316:

O = (1.974 ÷ 1.316) = 1.5 Cr = (1.316 ÷ 1.316) = 1

The ratio of Cr : O is 1 : 1.5.

Multiply by 2... 2 × (1 : 1.5) = 2 : 3.

So the empirical formula is $\mathbf{Cr_2O_3}$.

Page 65 — Application Questions

Q1 mass O in oxide = 7.1 – 3.1 = 4.0 g
moles O = mass ÷ M_r = 4.0 ÷ 16 = 0.25 mol
moles P = mass ÷ M_r = 3.1 ÷ 31 = 0.10 mol
So, the ratio of P : O = 0.10 : 0.25 = 2 : 5 and the empirical formula is $\mathbf{P_2O_5}$.
mass of empirical formula is (31 × 2) + (5 × 16) = 142 g mol^{-1}
284 ÷ 142 = 2 so the empirical formula is scaled up by a factor of 2 and the molecular formula is $\mathbf{P_4O_{10}}$.

Q2 Mass of each element:
C = 85.7 g H = 14.3 g
Moles of each element:
C = (85.7 ÷ 12) = 7.14 moles
H = (14.3 ÷ 1) = 14.3 moles
Divide each by 7.14:
C = (7.14 ÷ 7.14) = 1 O = (14.3 ÷ 7.14) = 2
The ratio of C : H is 1 : 2. So the empirical formula is CH_2.
mass of empirical formula is 12 + (2 × 1) = 14 g mol^{-1}.
56 ÷ 14 = 4 so the empirical formula is scaled up by a factor of 4 and the molecular formula is $\mathbf{C_4H_8}$.

Q3 Mass of each element:
Cl = 42.5 g O = 100 – 42.5 = 57.5 g
Moles of each element:
Cl = (42.5 ÷ 35.5) = 1.20 moles
O = (57.5 ÷ 16) = 3.59 moles
Divide each by 1.20:
Cl = (1.20 ÷ 1.20) = 1 O = (3.59 ÷ 1.20) = 3
The ratio of Cl : O is 1 : 3. So the empirical formula is ClO_3.
mass of empirical formula is 35.5 + (3 × 16) = 83.5 g mol^{-1}.
167 ÷ 83.5 = 2 so the empirical formula is scaled up by a factor of 2 and the molecular formula is $\mathbf{Cl_2O_6}$.

Q4 moles CO_2 = mass ÷ M_r = 17.6 ÷ 44 = 0.40 mol
moles H_2O = mass ÷ M_r = 14.4 ÷ 18 = 0.80 mol
There is 1 mole of C in 1 mol of CO_2 so you must have started with 0.40 moles of C.
There are 2 moles of H in 1 mol of H_2O so you must have started with 2 × 0.80 = 1.6 moles of H.
mass of C in alcohol = moles × M_r = 0.40 × 12 = 4.8 g
mass of H in alcohol = moles × M_r = 1.6 × 1 = 1.6 g
mass of O in alcohol = 12.8 – (4.8 + 1.6) = 6.4 g
moles O = mass ÷ M_r = 6.4 ÷ 16 = 0.40 mol
So, the ratio of C : H : O = 0.4 : 1.6 : 0.4 = 1 : 4 : 1 and the empirical formula is $\mathbf{CH_4O}$.
mass of empirical formula is 12 + (4 × 1) + 16 = 32 g mol^{-1}
32 ÷ 32 = 1 so the empirical formula is not scaled up and the molecular formula is $\mathbf{CH_4O}$.

Q5 moles CO_2 = mass ÷ M_r = 5.28 ÷ 44 = 0.12 mol
moles H_2O = mass ÷ M_r = 2.16 ÷ 18 = 0.12 mol
There is 1 mole of C in 1 mole of CO_2 so you must have started with 0.12 moles of C.
There are 2 moles of H in 1 mole of H_2O so you must have started with 2 × 0.12 = 0.24 moles of H.
mass of C in alcohol = moles × M_r = 0.12 × 12 = 1.44 g
mass of H in alcohol = moles × M_r = 0.24 × 1 = 0.24 g
mass of O in alcohol = 2.64 – (1.44 + 0.24) = 0.96 g
moles O = mass ÷ M_r = 0.96 ÷ 16 = 0.060 mol
So, the ratio of C : H : O = 0.12 : 0.24 : 0.060 = 2 : 4 : 1 and the empirical formula is $\mathbf{C_2H_4O}$.
mass of empirical formula is (12 × 2) + (4 × 1) + 16 = 44 g mol^{-1}. 88 ÷ 44 = 2 so the empirical formula is scaled up by a factor of 2 and the molecular formula is $\mathbf{C_4H_8O_2}$.

Page 65 — Fact Recall Questions

Q1 moles = mass ÷ M_r

Q2 The percentage composition tells you what percentage of the mass of the compound is made up of each element.

3. Chemical Equations

Page 67 — Application Questions

Q1 a) $Mg + \mathbf{2}HCl \rightarrow MgCl_2 + H_2$
b) $S_8 + \mathbf{24}F_2 \rightarrow \mathbf{8}SF_6$
c) $Ca(OH)_2 + H_2SO_4 \rightarrow CaSO_4 + \mathbf{2}H_2O$
d) $Na_2CO_3 + \mathbf{2}HCl \rightarrow \mathbf{2}NaCl + CO_2 + H_2O$
e) $C_4H_{10} + \mathbf{6\frac{1}{2}}O_2 \rightarrow \mathbf{4}CO_2 + \mathbf{5}H_2O$
If you wanted to double the numbers to get rid of the half in this equation that would be fine too (making it $2C_4H_{10} + 13O_2 \rightarrow 8CO_2 + 10H_2O$).

Q2 a) $Fe + Cu^{2+} \rightarrow Fe^{2+} + Cu$
b) $Ba^{2+} + SO_4^{2-} \rightarrow BaSO_4$
This reaction looks like it has the same ions on each side of the equation, so wouldn't have an ionic equation. But the state symbols show you that $BaSO_4$ is a solid, so you shouldn't split it up into ions when writing your ionic equation.
c) $CO_3^{2-} + 2H^+ \rightarrow H_2O + CO_2$

4. Equations and Calculations

Page 69 — Application Questions

Q1 a) $Zn + 2HCl \rightarrow ZnCl_2 + H_2$
b) M_r of Zn = 65.4
number of moles = mass ÷ M_r = 3.30 ÷ 65.4
= **0.0505 moles**
c) The molar ratio of Zn : $ZnCl_2$ is 1 : 1. So 0.0505 moles of Zn will give **0.0505 moles** of $ZnCl_2$.
d) M_r of $ZnCl_2$ = 65.4 + (2 × 35.5) = 136.4
mass = number of moles × M_r = 0.0505 × 136.4 = **6.89 g**

Q2 a) $C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$
b) M_r of H_2O = (2 × 1) + 16 = 18
number of moles = mass ÷ M_r = 15.0 ÷ 18 = **0.833 moles**
c) The molar ratio of H_2O : C_2H_4 is 2 : 1.
So 0.833 moles of H_2O must be made from (0.833 ÷ 2) = **0.417 moles** of C_2H_4.
d) M_r of C_2H_4 = (2 × 12) + (4 × 1) = 28
mass = number of moles × M_r = 0.417 × 28 = **11.7 g**

Q3 $Na_2CO_3 + BaCl_2 \rightarrow 2NaCl + BaCO_3$
M_r of $BaCl_2$ = 137.3 + (2 × 35.5) = 208.3
number of moles = mass ÷ M_r = 4.58 ÷ 208.3 = 0.0220 mol
The molar ratio of $BaCl_2$: $BaCO_3$ is 1 : 1.
So 0.0220 moles of $BaCO_3$ must be made from 0.0220 moles of $BaCl_2$.
M_r of $BaCO_3$ = 137.3 + 12 + (16 × 3) = 197.3
mass = number of moles × M_r = 0.0220 × 197.3 = **4.34 g**

Page 70 — Application Questions

Q1 a) aq
b) s
c) l
d) aq
e) g
f) s

Q2 a) $2H_2O_{(l)} \rightarrow 2H_{2(g)} + O_{2(g)}$
b) M_r of H_2O = (2 × 1) + 16 = 18
number of moles = mass ÷ M_r = 9.0 ÷ 18 = **0.50 moles**
c) The molar ratio of H_2O to O_2 is 2 : 1.
So 0.50 moles of H_2O will produce
(0.50 ÷ 2) = **0.25 moles** of O_2.
d) At room temperature and pressure 1 mole of gas takes up 24 dm^3.
Volume in dm^3 = number of moles × 24
Volume of O_2 = 0.25 × 24 = **6.0 dm^3**

Q3 a) $ZnS_{(s)} + 1½O_{2(g)} \rightarrow ZnO_{(s)} + SO_{2(g)}$
b) M_r of ZnS = 65.4 + 32.1 = 97.5
number of moles = mass ÷ M_r = 7.00 ÷ 97.5
= **0.0718 moles**
c) The molar ratio of ZnS to SO_2 is 1 : 1.
So 0.0718 moles of ZnS will give **0.0718 moles** of SO_2.
d) At room temperature and pressure 1 mole of gas takes up 24 dm^3.
Volume in dm^3 = number of moles × 24
Volume of SO_2 = 0.0718 × 24 = **1.72 dm^3**

Q4 a) $C_6H_{14(g)} \rightarrow C_4H_{10(g)} + C_2H_{4(g)}$
b) M_r of C_4H_{10} = (4 × 12) + (10 × 1) = 58
number of moles = mass ÷ M_r = 3.00 ÷ 58
= **0.0517 moles**
c) The molar ratio of C_4H_{10} to C_6H_{14} is 1 : 1.
So 0.0517 moles of C_4H_{10} must be made from **0.0517 moles** of C_6H_{14}.
d) At room temperature and pressure 1 mole of gas takes up 24 dm^3.
Volume in dm^3 = number of moles × 24
Volume of C_6H_{14} = 0.0517 × 24 = **1.24 dm^3**

Q5 $2Mg_{(s)} + O_{2(g)} \rightarrow 2MgO_{(s)}$
M_r of MgO = 24.3 + 16.0 = 40.3
number of moles = mass ÷ M_r = 10 ÷ 40.3 = 0.25 moles
The molar ratio of MgO : O_2 is 2 : 1.
So 0.25 moles of MgO is made from 0.125 moles of O_2.
At room temperature and pressure 1 mole of gas takes up 24 dm^3.
Volume in dm^3 = number of moles × 24
Volume of O_2 = 0.125 × 24 = **3.0 dm^3**

5. Formulas of Ionic Compounds

Page 72 — Application Questions

Q1 a) +1
b) +1
c) –1

Q2 Calcium is in group 2 so loses 2 electrons to form Ca^{2+} ions. Chlorine is in group 7 so gains 1 electron to form Cl^- ions. For every calcium ion, you need two chloride ions to balance the charge: (+2) + (–1 × 2) = 0. So the ratio of calcium to chloride ions is 1 : 2. The formula is **$CaCl_2$**.

Q3 a) +2
b) NO_3^-
c) $Zn(NO_3)_2$

Page 72 — Fact Recall Questions

Q1 +1
Q2 Carbon and oxygen.
Q3 +1

Exam-style Questions — pages 74–75

1 A *(1 mark)*
2 B *(1 mark)*
3 D *(1 mark)*

4 a) $2HCl + MgCO_3 \rightarrow CO_2 + H_2O + MgCl_2$ ***(1 mark)***
$2H^+ + 2Cl^- + Mg^{2+} + CO_3^{2-} \rightarrow CO_2 + H_2O + Mg^{2+} + 2Cl$
$2H^+ + CO_3^{2-} \rightarrow CO_2 + H_2O$ ***(1 mark)***
b) At r.t.p., moles = volume ÷ 24 000 (cm^3) ***(1 mark)***
= 496.3 ÷ 24 000 = 0.0206... mol ***(1 mark)***
From the balanced equation, 1 mole of $MgCO_3$ produced 1 mole of CO_2. So 0.0206... moles of CO_2 is produced by 0.0206... moles of $MgCO_3$ ***(1 mark)***.
M_r $MgCO_3$ = 24.3 + 12.0 + (16.0 × 3) = 84.3 g mol^{-1}
mass = moles × molar mass
= 0.0206... × 84.3 = **1.74 g** (3 s.f.) ***(1 mark)***

5 a) The empirical formula is a formula giving the simplest whole number ratio of atoms of each element present in a compound ***(1 mark)***.
b) (i) moles CO_2 = mass ÷ M_r = 17.6 ÷ 44 = **0.40 moles**
moles H_2O = mass ÷ M_r = 9.0 ÷ 18 = **0.50 moles**
(1 mark for each correct number of moles).
(ii) There is 1 mole of C in 1 mole of CO_2 so must have started with 0.40 moles of C.
mass C = moles × M_r = 0.40 × 12 = **4.8 g**
There are 2 moles of H in 1 mole of H_2O so must have started with 0.50 × 2 = 1.0 moles of H.
mass H = 1.0 × 1 = **1.0 g**
mass O = total mass – (mass of C + mass of H)
= 9 – (4.8 + 1.0) = **3.2 g**
(1 mark for each correct mass).
(iii) moles O = mass ÷ M_r = 3.2 ÷ 16 = 0.2 moles ***(1 mark)***. So the ratio of C : H : O = 0.4 : 1.0 : 0.2 = 2 : 5 : 1 so the empirical formula is **C_2H_5O** ***(1 mark)***.
c) (i) The molecular formula is a formula giving the actual number of atoms of each element present in a molecule ***(1 mark)***.
(ii) The formula mass of the empirical formula is (12 × 2) + (5 × 1) + 16 = 45 ***(1 mark)***.
90 ÷ 45 = 2 so the empirical formula is scaled up by a factor of 2 and the molecular formula is **$C_4H_{10}O_2$** ***(1 mark)***.

6 a) $Cl_2 + 2NaOH \rightarrow NaClO + NaCl + H_2O$ ***(1 mark)***
b) M_r of NaClO = 23 + 35.5 + 16 = 74.5 g mol^{-1}
moles NaClO = 37.1 ÷ 74.5 = 0.497... moles ***(1 mark)***
From the balanced equation, 2 moles of NaOH react to produce 1 mole of NaClO, so 0.995... moles of NaOH must react to produce 0.497... moles of NaClO ***(1 mark)***.
M_r NaOH = 23 + 16 + 1 = 40 g mol^{-1}
mass NaOH = 40 × 0.995... = **39.8 g** ***(1 mark)***
c) –1 ***(1 mark)***

7 a) NO_3^- ***(1 mark)***
b) In 100 g, 59.6 g will be O.
So moles O = 59.6 ÷ 16 = 3.725 moles ***(1 mark)***
For each mole of O, you must have:
3.725 ÷ 3 = 1.241... moles N ***(1 mark)***.
So % composition N = 1.241... × 14 = 17.38...%
So % composition of nitrate = 17.38... + 59.6
= 76.98...% ***(1 mark)***
So, % composition of iron = 100 – 76.98... = 23.01...%
So ratio of Fe : NO_3 =
(23.01... ÷ M_r(Fe)) : (76.98... ÷ M_r(NO_3)) = 1 : 3 ***(1 mark)***
Therefore the formula of the iron nitrate is **$Fe(NO_3)_3$** ***(1 mark)***.

Section 3 — Reactions and Calculations

1. Acids, Bases and Salts

Page 80 — Application Questions

Q1 a) $CuO_{(s)} + 2HCl_{(aq)} \rightarrow CuCl_{2(aq)} + H_2O_{(l)}$
b) $NaOH_{(aq)} + HCl_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(l)}$

Don't forget to balance your equations. You'll lose marks in the exam if you don't.

Q2 a) $2Fe_{(s)} + 3H_2SO_{4(aq)} \rightarrow Fe_2(SO_4)_{3(aq)} + 3H_{2(g)}$
b) $CaCO_{3(s)} + H_2SO_{4(aq)} \rightarrow CaSO_{4(aq)} + CO_{2(g)} + H_2O_{(l)}$
Q3 a) $Al_2O_{3(s)} + 6HNO_{3(aq)} \rightarrow 2Al(NO_3)_{3(aq)} + 3H_2O_{(l)}$
b) $KOH_{(aq)} + HNO_{3(aq)} \rightarrow KNO_{3(aq)} + H_2O_{(l)}$
c) $MgCO_{3(s)} + 2HNO_{3(aq)} \rightarrow Mg(NO_3)_{2(aq)} + H_2O_{(l)} + CO_{2(g)}$

Page 80 — Fact Recall Questions

Q1 a) A substance that releases H^+ ions in aqueous solution (a proton donor).
b) A substance that removes H^+ ions from an aqueous solution (a proton acceptor).
Q2 a) An acid that almost completely ionises/dissociates in an aqueous solution.
b) A base that only slightly ionises/dissociates in an aqueous solution.
Q3 a) HCl
b) H_2SO_4
c) HNO_3
d) NaOH
e) KOH
f) NH_3
Q4 a) chloride
b) sulfate
c) nitrate
Q5 a) A salt and water.
b) A salt, carbon dioxide and water.
c) A salt and hydrogen.

2. Anhydrous and Hydrated Salts

Page 82 — Application Questions

Q1 mass H_2O in hydrated salt = 57.5 – 32.3 = 25.2 g
This is the mass of the hydrated salt minus the mass of the anhydrous salt.
moles $ZnSO_4$ = mass ÷ M = 32.3 ÷ 161.5 = 0.20 mol
moles H_2O = mass ÷ M = 25.2 ÷ 18 = 1.4 mol
So, the ratio of $ZnSO_4$: H_2O in the hydrated salt = 0.20 : 1.4 = 1 : 7 so **X = 7** and the formula of the hydrated salt is **$ZnSO_4.7H_2O$**.
Q2 mass $CoCl_2$ in hydrated salt = 35.685 – 16.200 = 19.485 g
This is the mass of the hydrated salt minus the mass of the water in the hydrated salt.
moles $CoCl_2$ = mass ÷ M = 19.485 ÷ 129.9 = 0.1500 mol
moles H_2O = mass ÷ M = 16.2 ÷ 18 = 0.90 mol
So, the ratio of $CoCl_2$: H_2O in the hydrated salt = 0.1500 : 0.90 = 1 : 6 so **X = 6** and the formula of the hydrated salt is **$CoCl_2.6H_2O$**.
Q3 % mass $BaCl_2$ = 100 – 14.74 = 85.26%.
Assuming you have 100 g of hydrated salt it would contain 85.26 g of $BaCl_2$ and 14.74 g of water.
moles $BaCl_2$ = mass ÷ M = 85.26 ÷ 208.3 = 0.41 mol
moles H_2O = mass ÷ M = 14.74 ÷ 18 = 0.82 mol
So, the ratio of $BaCl_2$: H_2O in the hydrated salt = 0.41 : 0.82 = 1 : 2 so the formula of the hydrated salt is **$BaCl_2.2H_2O$**.
Q4 % mass $Fe(NO_3)_3$ = 100 – 30.87 = 69.13%.
Assuming you have 100 g of hydrated salt it would contain 69.13 g of $Fe(NO_3)_3$ and 30.87 g of water.
moles $Fe(NO_3)_3$ = mass ÷ M = 69.13 ÷ 241.8 = 0.290 mol
moles H_2O = mass ÷ M = 30.87 ÷ 18 = 1.72 mol
So, the ratio of $Fe(NO_3)_3$: H_2O in the hydrated salt = 0.290 : 1.72 = 1 : 6 and so the formula of the hydrated salt is **$Fe(NO_3)_3.6H_2O$**.

Page 82 — Fact Recall Questions

Q1 Water of crystallisation.
Q2 Anhydrous means that a substance doesn't contain water of crystallisation.
Q3 By heating — hydrated salts lose their water of crystallisation and become anhydrous when they are heated.

3. Titrations

Page 86 — Application Questions

Q1 moles NaCl = 1.50 × (400 ÷ 1000) = **0.600 moles**
Q2 moles $NaHSO_4$ = 2.0 × (250 ÷ 1000) = **0.50 moles**
Q3 moles $H_2C_2O_4$ = 1.250 × (500.0 ÷ 1000) = 0.6250 moles
M_r $H_2C_2O_4$ = (2 × 1) + (2 × 12) + (4 × 16) = 90 g mol^{-1}
mass $H_2C_2O_4$ = 0.6250 × 90 = **56.25 g**
Q4 a) 0.400 ÷ 1.60 = 0.250
0.250 × 250 = **62.5 cm^3**
b) 250 – 62.5 = **187.5 cm^3**
Q5 Volume of stock HCl solution required: 1.50 ÷ 5.00 = 0.300
0.300 × 100 = 30 cm^3 of 5.00 mol dm^{-3} solution
Volume of distilled water required: 100 – 30 = 70 cm^3.
So, to make the 1.50 mol dm^{-3} solution, you would mix **30 cm^3 of 5.00 mol dm^{-3} HCl solution** with **70 cm^3 distilled water**.

Page 86 — Fact Recall Questions

Q1 A burette.
Q2 E.g. methyl orange and phenolphthalein.
Q3 A solution that has a precisely known concentration.

4. Titration Calculations

Page 88 — Application Questions

Q1 a) $HCl_{(aq)} + KOH_{(aq)} \rightarrow KCl_{(aq)} + H_2O_{(l)}$

b) moles HCl = (conc. × volume (cm^3)) ÷ 1000
= (0.750 × 28) ÷ 1000 = **0.0210 moles**

c) 1 mole of HCl reacts with 1 mole of KOH.
So 0.0210 moles of HCl must react with **0.0210 moles** of KOH.

d) concentration = (moles KOH × 1000) ÷ vol. (cm^3)
= (0.0210 × 1000) ÷ 40.0 = **0.525 mol dm^{-3}**

Q2 $NaOH_{(aq)} + HNO_{3\,(aq)} \rightarrow NaNO_{3\,(aq)} + H_2O_{(l)}$
moles NaOH = (conc. × volume (cm^3)) ÷ 1000
= (1.50 × 15.3) ÷ 1000 = 0.02295 moles
1 mole of NaOH reacts with 1 mole of HNO_3.
So 0.02295 moles of NaOH must react with 0.02295 moles of HNO_3.
concentration = (moles HNO_3 × 1000) ÷ vol. (cm^3)
= (0.02295 × 1000) ÷ 35.0 = **0.656 mol dm^{-3}**

Q3 $LiOH_{(aq)} + HCl_{(aq)} \rightarrow LiCl_{(aq)} + H_2O_{(l)}$
moles HCl = (conc. × volume (cm^3)) ÷ 1000
= (0.500 × 12.0) ÷ 1000 = 0.00600 moles
1 mole of HCl reacts with 1 mole of LiOH, so 0.00600 moles of HCl must react with 0.00600 moles of LiOH.
concentration = (moles LiOH × 1000) ÷ vol. (cm^3)
= (0.00600 × 1000) ÷ 24.0 = **0.250 mol dm^{-3}**

Page 89 — Application Questions

Q1 a) $HNO_3 + LiOH \rightarrow LiNO_3 + H_2O$

b) moles HNO_3 = (conc. × volume (cm^3)) ÷ 1000
= (0.200 × 18.8) ÷ 1000 = **0.00376 moles**

c) 1 mole of HNO_3 reacts with 1 mole of LiOH.
So 0.00376 moles of HNO_3 must react with **0.00376 moles** of LiOH.

d) volume = (moles LiOH × 1000) ÷ concentration
= (0.00376 × 1000) ÷ 0.450 = **8.36 cm^3**

Q2 a) $KOH + CH_3COOH \rightarrow CH_3COOK + H_2O$

b) moles KOH = (conc. × volume (cm^3)) ÷ 1000
= (0.420 × 37.3) ÷ 1000 = **0.0157 moles**

c) 1 mole of KOH reacts with 1 mole of CH_3COOH.
So 0.0157 moles of KOH must react with 0.0157 moles of CH_3COOH.
volume = (moles CH_3COOH × 1000) ÷ conc.
= (0.0157 × 1000) ÷ 1.10 = **14.3 cm^3**

Q3 $Ba(OH)_2 + 2HCl \rightarrow BaCl_2 + 2H_2O$
moles of $Ba(OH)_2$ = (conc. × volume (cm^3)) ÷ 1000
= (14 × 1) ÷ 1000 = 0.014 moles
1 mole of $Ba(OH)_2$ reacts with 2 moles of HCl. So, 0.014 moles of $Ba(OH)_2$ must react with 0.028 moles of HCl.
volume of HCl = (moles HCl × 1000) ÷ conc.
= (0.028 × 1000) ÷ 0.50 = **56 cm^3**

5. Chemical Yield

Page 91 — Application Questions

Q1 % yield = (actual yield ÷ theoretical yield) × 100
= (1.76 ÷ 3.24) × 100 = **54.3%**

Q2 % yield = (actual yield ÷ theoretical yield) × 100
= (3.70 ÷ 6.10) × 100 = **60.7%**

Q3 a) Molar mass of $(CH_3CO)_2O$ = 2 × ((12 + (3 × 1) + 12 + 16)) + 16 = 102 g mol^{-1}
Number of moles $(CH_3CO)_2O$ = mass ÷ molar mass
= 3.00 ÷ 102 = **0.0294 moles**

b) From the equation: 1 mole of $(CH_3CO)_2O$ produces 2 moles of CH_3COOH, so 0.0294 moles of $(CH_3CO)_2O$ will produce (0.0294 × 2) = 0.0588 moles of CH_3COOH.
Molar mass of CH_3COOH
= 12 + (3 × 1) + 12 + 16 + 16 + 1 = 60 g mol^{-1}
Theoretical yield = moles CH_3COOH × molar mass
= 0.0588 × 60 = **3.53 g**

c) % yield = (actual yield ÷ theoretical yield) × 100
= (2.80 ÷ 3.53) × 100 = **79.3%**

Q4 a) Molar mass of CH_3CHCH_2 =
12 + (3 × 1) + 12 + 1 + 12 + (2 × 1) = 42 g mol^{-1}
Number of moles CH_3CHCH_2 = mass ÷ molar mass
= 50 ÷ 42 = 1.19... moles
From the equation: 1 mole of CH_3CHCH_2 produces 1 mole of $CH_3CH_2CH_2Cl$, so 1.19 ... moles of CH_3CHCH_2 will produce 1.19 ... moles of $CH_3CH_2CH_2Cl$.
Molar mass of $CH_3CH_2CH_2Cl$
= 12 + (3 × 1) + 12 + (2 × 1) + 12 + (2 × 1) + 35.5
= 78.5 g mol^{-1}
Theoretical yield = moles $CH_3CH_2CH_2Cl$ × molar mass
= 1.19 ... × 78.5 = **93.5 g**

b) % yield = (actual yield ÷ theoretical yield) × 100
= (54 ÷ 93.5) × 100 = **57.8%**

Q5 Molar mass of HCOOH = 1 + 12 + 16 + 16 + 1 = 46 g mol^{-1}
Number of moles HCOOH = mass ÷ molar mass
= 4.70 ÷ 46 = 0.102... moles
From the equation: 2 moles of HCOOH produce 1 mole of $(CHO)_2O$, so 0.102... moles of NaOH will produce (0.102... ÷ 2) = 0.0510... moles of $(CHO)_2O$.
Molar mass of $(CHO)_2O$ = (2 × (12 + 1 + 16)) + 16 = 74 g mol^{-1}
Theoretical yield = moles $(CHO)_2O$ × molar mass
= 0.0510... × 74 = 3.78 g
% yield = (actual yield ÷ theoretical yield) × 100
= (3.60 ÷ 3.78...) × 100 = **95.2%**

Page 91 — Fact Recall Questions

Q1 The theoretical yield is the mass of product that should be formed in a chemical reaction, assuming no chemicals are 'lost' in the process.

Q2 $$\text{percentage yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100$$

6. Atom Economy

Page 94 — Application Questions

Q1 a) mass of CH_3Cl = 12 + (3 × 1) + 35.5 = **50.5**

b) mass of products = (12 + (3 × 1) + 35.5) + (1 + 35.5) = **87**

c) $$\% \text{ atom economy} = \frac{M_r \text{ of desired product}}{\text{Total mass of all products}} \times 100$$

= (50.5 ÷ 87) × 100 = **58.0%**

d) E.g. sell the HCl so it can be used in other chemical reactions / use the HCl as a reactant in another reaction.

Q2 mass of product = (2 × 12) + (5 × 1) + 16 + 1 = 46

$$\% \text{ atom economy} = \frac{M_r \text{ of desired product}}{\text{Total mass of all products}} \times 100$$

= (46 ÷ 46) × 100 = **100%**

Award yourself an extra chocolate biscuit if you spotted that this reaction has 100% atom economy before you did the calculations — any reaction where there's only one product will have 100% atom economy.

Q3 mass of C_2H_4 = (2 × 12) + (4 × 1) = 28

mass of H_2O = (2 × 1) + 16 = 18

total mass of products = 28 + 18 = 46

$$\% \text{ atom economy} = \frac{M_r \text{ of desired product}}{\text{Total mass of all products}} \times 100$$

= (28 ÷ 46) × 100 = **60.9%**

Q4 a) Reaction 1:

total mass of products = 2 × (14 + (3 × 1)) = 34

$$\% \text{ atom economy} = \frac{M_r \text{ of desired product}}{\text{Total mass of all products}} \times 100$$

= (34 ÷ 34) × 100 = **100%**

Reaction 2:

mass of $CaCl_2$ = 40.1 + (35.5 × 2) = 111.1

mass of $2NH_3$ = 2 × (14 + (3 × 1)) = 34

mass of $2H_2O$ = 2 × ((2 × 1) + 16) = 36

total mass of products = 181.1

$$\% \text{ atom economy} = \frac{M_r \text{ of desired product}}{\text{Total } M_r \text{ of all products}} \times 100$$

= (34 ÷ 181.1) × 100 = **18.8%**

b) E.g. reaction 1 has a much higher atom economy / produces no waste.

Page 94 — Fact Recall Questions

Q1 Atom economy is a measure of the proportion of reactant atoms that become part of the desired product (rather than by-products) in the balanced chemical equation.

Q2 $$\% \text{ atom economy} = \frac{M_r \text{ of desired product}}{\text{Total } M_r \text{ of all products}} \times 100$$

Q3 Any two from: e.g. for low atom economy reactions there's lots of waste produced / it costs money to separate the desired product from waste / it costs money to dispose of waste products safely / reactant chemicals are expensive so it wastes money if a high proportion of them end up as useless products / high atom economy reactions are more sustainable.

7. Oxidation Numbers

Page 98 — Application Questions

Q1 a) +1

b) –1

c) +2

Q2 a) –1

b) –2

c) –1

Q3 a) H: +1, Cl: –1

b) C: +4, O: –2

c) Cl: +7, O: –2

d) H: +1, S: +6, O: –2

Oxygen has an oxidation number of –2. There are 4 oxygen atoms here so the total is –8. The overall oxidation number of the ion is –1. Hydrogen has an oxidation number of +1. So, sulfur must have an oxidation number of +6 (as –8 + 1 + 6 = –1).

Q4 a) +2

b) +4

c) +4

Calcium forms Ca^{2+} ions so has an oxidation number of +2. Oxygen has an oxidation number of –2. There are 3 oxygen atoms here so the total is –6. The overall oxidation number of the compound is 0. So, carbon must have an oxidation number of +4 (as –6 + 4 = –2).

d) –2

Hydrogen has an oxidation number of +1. So, in C_3H_6, carbon must have an oxidation number of –2 (as (6 x +1) + (3 x –2) = 0).

Q5 a) 0

b) –3

c) +6

d) +2

Fluorine is the most electronegative element so its oxidation number is equal to its ionic charge, –1. There are 4 fluorine atoms here so the total is –4. So, phosphorus must have an oxidation number of +2 (as (4 x –1) + (2 x +2) = 0).

Q6 a) +3

b) +7

Q7 a) iron(II) sulfate

b) manganese(II) carbonate

c) copper(II) oxide

Q8 a) $CuSO_4$

b) FeO

c) NO_2^-

d) CrO_4^{2-}

Page 98 — Fact Recall Questions

Q1 0

Q2 0

Q3 –1

Q4 –1

8. Redox Reactions

Page 101 — Application Questions

Q1 a) The oxidation number of magnesium increases from 0 to +2. The oxidation number of hydrogen decreases from +1 to 0.

b) The oxidation number of vanadium increases from 0 to +3. The oxidation number of hydrogen decreases from +1 to 0.

c) The oxidation number of iron increases from 0 to +3. The oxidation number of hydrogen decreases from +1 to 0.

Q2 a) The oxidation number of manganese decreases from +4 to +2. The oxidation number of two of the chlorine atoms increases from –1 to 0.

Only two of the chlorine atoms show an increase in oxidation number. The other two stay with an oxidation number of –1.

b) MnO_2 is the oxidising agent. It accepts electrons and gets reduced. HCl is the reducing agent. It donates electrons and gets oxidised.

Page 101 — Fact Recall Questions

Q1 Oxidation is a loss of electrons.

Q2 Reduction is a gain of electrons.

Q3 An oxidising agent accepts electrons from another reactant and is reduced.

Q4 A reducing agent donates electrons to another reactant and is oxidised.

Q5 It increases by 1.

Q6 It decreases by 1.

Exam-style Questions — pages 103–105

1 D ***(1 mark)***

2 C ***(1 mark)***

3 A ***(1 mark)***

4 a) (i) +4 ***(1 mark)***

(ii) silicon(IV) oxide ***(1 mark)***

b) This is not a redox reaction ***(1 mark)***. There are no changes in oxidation state during this reaction ***(1 mark)***.

5 a) (i) $Zn_{(s)} + 2HCl_{(aq)} \rightarrow ZnCl_{2\,(aq)} + H_{2\,(g)}$ ***(1 mark for correct balanced equation, 1 mark for correct state symbols)***

(ii) atom economy = M_r desired product ÷ M_r all products × 100%

= (2 × 1) ÷ ((2 × 1) + (65.4 + (35.5 × 2)) × 100% ***(1 mark)***

= **1.45%** ***(1 mark)***

b) (i) (3 × (2 × 1)) ÷ ((3 × (2 × 1)) + (12 + 16)) × 100% ***(1 mark)*** = **17.6%** ***(1 mark)***

(ii) Any two from: e.g. Steam reformation has a higher atom economy. This means it's more sustainable/ less waste is produced. / It costs money to dispose of waste products. / Reagents are often expensive, so it's wasteful if a high proportion of them are converted to waste products. ***(2 marks — 1 mark for each appropriate reason.)***

6 a) (i) Water of crystallisation is the water contained in an ionic lattice ***(1 mark)***.

(ii) A salt is hydrated if it contains water of crystallisation***(1 mark)***.

(iii) A salt is anhydrous if it doesn't contain any water of crystallisation ***(1 mark)***.

b) +2 ***(1 mark)***

c) mass of water lost = 8.93 – 4.88 = 4.05 g

moles of water lost = 4.05 ÷ (16 + (2 × 1)) = 0.225 mol ***(1 mark)***

M_r $FeSO_4$ = 55.8 + 32.1 + (16 × 4) = 151.9

moles of anhydrous $FeSO_4$ = 4.88 ÷ 151.9 = 0.0321 mol ***(1 mark)***

ratio of H_2O : $FeSO_4$ = 0.225 : 0.0321

(divide by 0.0321) = 7 : 1, so **x** = 7.

So formula for hydrated iron(II) sulfate is $\mathbf{FeSO_4{\bullet}7H_2O}$ ***(1 mark)***

7 a) (i) $HCl_{(aq)} + NaOH_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(l)}$

(1 mark for correct balanced equation, 1 mark for correct state symbols)

(ii) moles HCl = (concentration × volume) ÷ 1000

= (0.6 × 26) ÷ 1000 = **0.0156 moles**.

(2 marks for correct answer, otherwise 1 mark for correct method if answer incorrect)

(iii) From the equation you know that 1 mole of HCl reacts with 1 mole of NaOH. So 0.0156 moles of HCl must react with 0.0156 moles of NaOH.

concentration of NaOH = (moles ÷ volume) × 1000

= (0.0156 ÷ 20) × 1000 = **0.78 mol dm^{-3}**

(2 marks for correct answer, otherwise 1 mark for correct method if answer incorrect)

If you get a question like this where you need your answer to the previous part of a question to answer it, you'll get the marks if everything you've done is right, even if you don't get the right answer because you made an error in the earlier part of the question.

b) (i) +3 ***(1 mark)***

(ii) $AlCl_3$ ***(1 mark)***

Cl forms Cl ions so has an oxidation number of –1. The overall oxidation number of aluminium chloride is 0 and aluminium has an oxidation number of +3, so there must be 3 Cl^- ions and the formula must be $AlCl_3$.

c) (i) The oxidation number of sodium increases from 0 to +1 ***(1 mark)***.

(ii) It is a reducing agent ***(1 mark)***.

d) Assuming there was 100 g of hydrated calcium nitrate, 30.5 g would be water and 100 – 30.5 = 69.5 g would be calcium nitrate ***(1 mark)***. moles water = mass ÷ M = 30.5 ÷ 18 = 1.694 mol ***(1 mark)***.

M of $Ca(NO_3)_2$ = 40.1 + [2 × (14 + (3 × 16))] = 164.1.

moles $Ca(NO_3)_2$ = mass ÷ M = 69.5 ÷ 164.1 = 0.424 mol ***(1 mark)***.

$Ca(NO_3)_2$: H_2O = 0.424 : 1.694 = 1 : 4 so **x = 4** ***(1 mark)***.

e) The student should have added dissolved calcium(II) nitrate to the volumetric flask, and then topped up the total volume to 250 cm^3 ***(1 mark)***. The student's solution will be too dilute ***(1 mark)***.

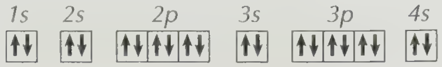
Section 4 — Electrons, Bonding and Structure

1. Electronic Structure

Page 109 — Application Questions

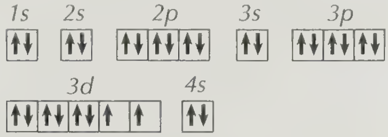
Q1 a) $1s^2\ 2s^1$
b) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^2\ 4s^2$
c) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^1$
d) $1s^2\ 2s^2\ 2p^3$

Q2 a)

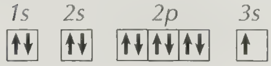


Remember — the 4s sub-shell has a lower energy level than the 3d sub-shell even though its principal quantum number is bigger. This means the 4s sub-shell fills up first.

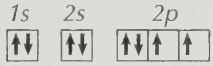
b)



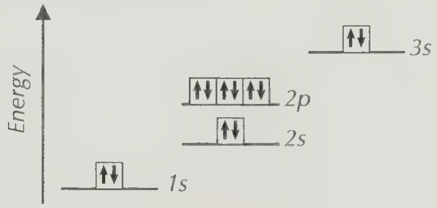
c)



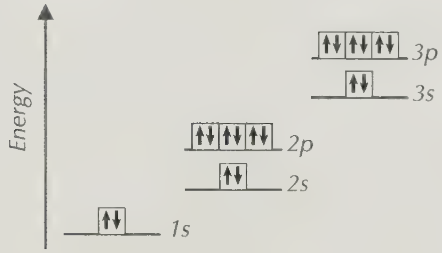
d)



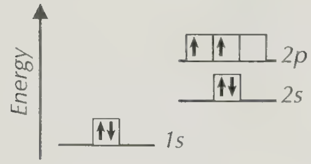
Q3 a)



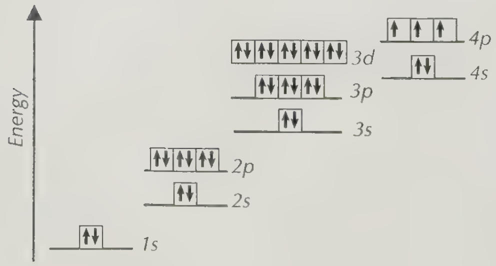
b)



c)



d)



Q4 a) $1s^2\ 2s^2\ 2p^6$
b) $1s^2\ 2s^2\ 2p^6$
c) $1s^2\ 2s^2\ 2p^6$
d) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$

Q5 a) bromine
b) phosphorus
c) vanadium

Page 109 — Fact Recall Questions

Q1 3

Q2 6 (it can hold two electrons in each orbital)

Q3 18

Q4 a) spherical
b) dumbbell-shaped

Q5 The number of electrons that an atom or ion has and how they are arranged.

Q6 The shells with the lowest energy (e.g. 1s then 2s then 2p etc.).

Q7 Electrons fill orbitals singly before they start sharing, so the two electrons in the 2p sub-shell should be in separate orbitals.

2. Ionic Bonding

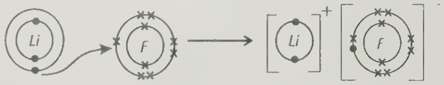
Page 112 — Application Questions

Q1 a) LiF

The lithium has a +1 charge and the fluoride ion has a −1 charge. To balance each other out and make a neutral ionic compound, you only need one of each ion.

b) A lithium atom (Li) loses 1 electron to form a lithium ion (Li^+). The fluorine atom (F) gains 1 electron to form a fluoride ion (F^-). Electrostatic attraction holds the positive and negative ions together — this is an ionic bond.

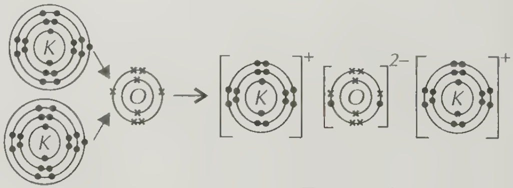
c)



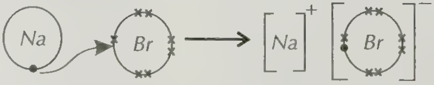
Q2 a) +1

The ionic formula is K_2O, and the charge on the oxide ion is −2. So the two potassium ions must have a combined charge of +2 to balance out the −2 charge and make the compound neutral. This means each potassium ion will have a charge of +2 ÷ 2 = +1.

b)



Q3

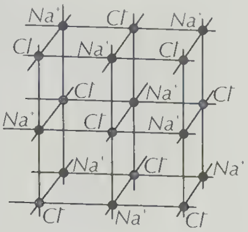


Page 112 — Fact Recall Questions

Q1 It holds positive and negative ions together.

Q2 A regular structure made up of ions.

Q3



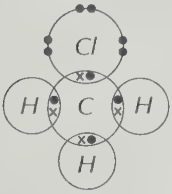
Q4 The ions in a molten ionic compound are free to move (and they carry a charge).

Q5 It will have a high melting point and a high boiling point. It will dissolve in water.

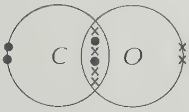
3. Covalent Bonding

Page 115 — Application Questions

Q1



Q2

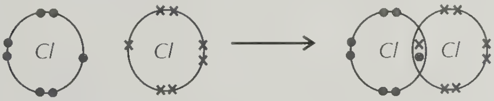


The overlapping region contains six electrons as it's a triple bond. Two of the electrons come from carbon, one for each of the normal covalent bonds, and four come from oxygen — one for each of the two normal covalent bonds, and an extra two for the dative covalent bond.

Page 115 — Fact Recall Questions

Q1 A covalent bond is the electrostatic attraction between a shared pair of electrons and the nuclei of the bonded atoms.

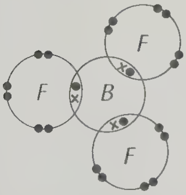
Q2



Q3 It is a covalent bond formed when two atoms share three pairs of electrons.

Q4 In a normal single covalent bond, one of the electrons in the shared pair of electrons comes from each atom. In a dative covalent bond, one of the atoms provides both of the shared electrons.

Q5



Q6 Average bond enthalpy tells you how strong a covalent bond is / how much energy is required to break a covalent bond.

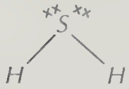
4. Shapes of Molecules

Page 119 — Application Questions

Q1 a) Sulfur has 6 outer electrons and 2 hydrogen atoms donate one electron each. So there are 8 electrons on the S atom, which is **4** electron pairs.

b) 2 electron pairs are involved in bonding, so there are **2** lone pairs.

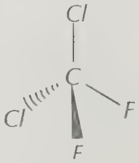
c)



non-linear

d) 104.5°

Q2



The shape is tetrahedral.
Carbon has 4 outer electrons and 2 chlorine and 2 fluorine atoms donate one electron each. So there are 8 electrons on the C atom, which is 4 electron pairs. All the electron pairs are involved in bonding and repel each other as much as possible, resulting in a tetrahedral shape.

Q3 Atom A: shape: trigonal planar, bond angle: 120°

The carbon atom has 4 outer electrons. The two hydrogens donate one electron each and the adjacent carbon atom donates 2 electrons as it forms a double bond. So there are 8 electrons on the C atom, which is 4 electron pairs. All the electron pairs are involved in bonding. The double bond means that the shape is based on a molecule with three electron pairs surrounding the central atom, i.e. trigonal planar, where the bond angles are 120°.

Atom B: shape: tetrahedral, bond angle: 109.5°

The carbon atom has 4 outer electrons and each of the two hydrogen atoms and the oxygen and adjacent carbon atoms donate one electron. So there are 8 electrons on the C atom, which is 4 electron pairs. All the electron pairs are involved in bonding so the shape is tetrahedral and the bond angles are 109.5°.

Atom C: shape: non-linear, bond angle: 104.5°

The oxygen atom has 6 outer electrons and the hydrogen and carbon atoms donate one electron each. So there are 8 electrons on the O atom, which is 4 electron pairs. Only two of the electron pairs are involved in bonding so there are two lone pairs. The shape is non-linear and the bond angle is 104.5°.

Page 119 — Fact Recall Questions

Q1 120°

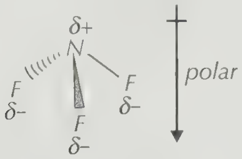
Q2 octahedral

5. Polarisation

Page 122 — Application Questions

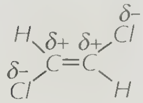
Q1 a) A C–O bond will have a permanent dipole.
b) An N–Cl bond will not have a permanent dipole.
c) A B–F bond will have a permanent dipole.

Q2 a)



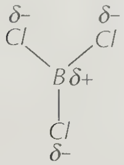
The molecule is polar.

b)



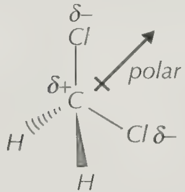
The polar C–Cl bonds point in opposite directions, so the molecule has no overall dipole and is non-polar.

Q3 a)



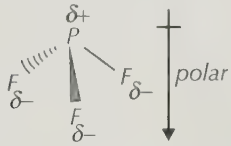
The polar B–Cl bonds cancel each other out, so the molecule has no overall dipole and is non-polar.

b)



The permanent dipoles on the two C–Cl bonds don't cancel each other out, so the molecule has an overall dipole and is polar.

c)



The permanent dipoles on the three P–F bonds don't cancel each other out, so the molecule has an overall dipole moment and is polar.

Page 122 — Fact Recall Questions

Q1 Electronegativity is the ability to attract the bonding electrons in a covalent bond. So a chlorine atom is better able to attract the electrons than a hydrogen atom.

Q2 Fluorine is more electronegative than hydrogen so attracts the electrons in the H—F covalent bond more than hydrogen. The bonding electrons are pulled towards the fluorine atom. This makes the bond polar.

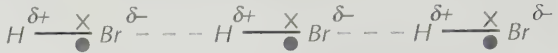
Q3 A dipole is a difference in charge between two atoms caused by a shift in the electron density in the bond between them.

6. Intermolecular Forces

Page 127 — Application Questions

Q1 Induced dipole-dipole interactions

Q2



Q3 a) Oxygen is more electronegative than chlorine so it has a greater ability to pull the bonding electrons away from hydrogen atoms. So the bonds are more polarised in H_2O than in HCl, which means that hydrogen bonds form in H_2O but not in HCl.
b) H_2O molecules are able to form hydrogen bonds whilst HCl only forms induced dipole-dipole forces and permanent dipole-dipole forces. Hydrogen bonds are the strongest type of intermolecular force, and therefore require more energy to break, so water has a higher boiling point than hydrogen chloride.
c) fluorine/F
d) carbon/C

Q4 a) NH_3 has hydrogen bonds between molecules whereas PH_3 only has induced dipole-dipole interactions, as the electronegativity values of P and H are very similar. It takes less energy to break induced dipole-dipole interactions than hydrogen bonds so the boiling point of PH_3 is lower.
b) lower

Q5 CH_4, CH_3Cl, CH_3I, CH_3OH
CH_4 has the lowest boiling point because it is a non-polar molecule so the molecules are only held together by induced dipole-dipole interactions. It also has the smallest electron cloud, so its induced dipole-dipole interactions are the weakest. CH_3Cl is a polar molecule so is able to form permanent dipole-dipole interactions as well as induced dipole-dipole interactions. Although CH_3I is less polar than CH_3Cl, and so the permanent dipole-dipole interactions are weaker, it has a larger electron cloud and so the induced dipole-dipole interactions are stronger, and overall the boiling point is greater. CH_3OH contains an -OH group which is able to form strong hydrogen bonds, and so has the highest boiling point.

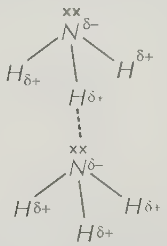
Page 127 — Fact Recall Questions

Q1 Induced dipole-dipole interactions / London (dispersion) forces, permanent dipole-dipole interactions and hydrogen bonds.

Q2 There are covalent bonds within iodine molecules and induced dipole-dipole interactions between iodine molecules. The intermolecular forces mean that iodine forms a simple molecular lattice.

Q3 Permanent dipole-dipole interactions are weak electrostatic forces of attraction between polar molecules.

Q4 a) hydrogen bonding
b)



Q5 Ice has more hydrogen bonds than liquid water, and hydrogen bonds are relatively long. So the H_2O molecules in ice are further apart on average, making ice less dense than liquid water.

Q6 a) Water is a polar molecule so only tends to dissolve other polar substances well. Chlorine isn't polar so is only slightly soluble in water.
b) No — chlorine wouldn't conduct electricity because there are no free ions to carry the charge.

Exam-style Questions — pages 129–131

Q1 B ***(1 mark)***

Q2 B ***(1 mark)***

Q3 D ***(1 mark)***

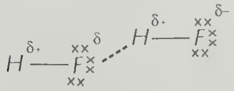
Q4 C ***(1 mark)***

Q5 a) (i) Electronegativity is the ability of an atom to attract the bonding electrons in a covalent bond ***(1 mark)***.

(ii) If there's a difference in the electronegativities of two covalently bonded atoms there's a shift in the electron density towards the more electronegative atom, making the bond polar ***(1 mark)***. This creates a dipole and causes weak electrostatic forces of attraction between molecules ***(1 mark)***.

b) (i) HCl: permanent dipole-dipole interactions and induced dipole-dipole interactions ***(1 mark)***
CH_4: induced dipole interactions ***(1 mark)***
HF: hydrogen bonds, permanent dipole-dipole interactions and induced dipole-dipole interactions ***(1 mark)***

(ii)



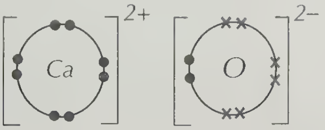
(3 marks — 1 mark for showing all lone pairs, 1 mark for showing the partial charges and 1 mark for showing the hydrogen bond going from a lone pair on an F atom to an H atom.)

(iii) The Cl atoms in Cl_2 have equal electronegativities so the covalent bond is non-polar ***(1 mark)***.

Q6 a) (i) An ionic bond is an electrostatic attraction between two oppositely charged ions ***(1 mark)***.

(ii) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$ ***(1 mark)***

(iii)



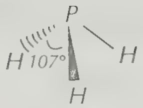
(2 marks — 1 mark for showing the correct number of outer electrons, 1 mark for showing the correct charges.)

b) Carbon dioxide is linear with a bond angle of 180° ***(1 mark)***. The molecule has two double bonds and no lone pairs on the central atom ***(1 mark)*** and the bonding pairs repel each other as much as possible ***(1 mark)***.

c) Calcium oxide will have a higher boiling point ***(1 mark)***. The ionic bonds in calcium oxide are much stronger than the induced dipole-dipole interactions that form between the molecules in carbon dioxide, so will require more energy to break ***(1 mark)***.

Q7 a) Going from PH_3 to SbH_3, the molecules have more electrons in them ***(1 mark)*** so the induced dipole-dipole interactions between the molecules increase in strength ***(1 mark)***. It takes more energy to break stronger induced dipole-dipole interactions so the boiling points increase from PH_3 to SbH_3 ***(1 mark)***. The boiling point of NH_3 doesn't follow this trend and is higher than expected because NH_3 is able to form strong hydrogen bonds between the molecules, which take more energy to break than induced dipole-dipole interactions ***(1 mark)***.

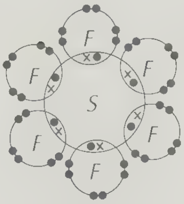
b)



(2 marks — 1 mark for correct shape, 1 mark for correct bond angle.)

c) NH_3 is the only one of the Group 5 hydrides that can form hydrogen bonds with the water molecules ***(1 mark)***. This allows for better mixing of the NH_3 molecules with water molecules than for the rest of the Group 5 hydrides ***(1 mark)***.

Q8 a)



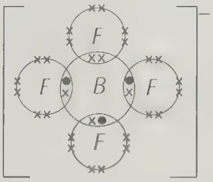
(1 mark)

The molecule has 6 bonding pairs of electrons on the central atom and these repel each other equally ***(1 mark)***. This means that all the angles between the bonding pairs are 90° ***(1 mark)*** and the shape is octahedral ***(1 mark)***.

b) (i) 120° ***(1 mark)***

(ii) A covalent bond formed between two atoms where one of the atoms provides both of the shared electrons ***(1 mark)***.

(iii)



(1 mark)

(iv) The shape will be tetrahedral ***(1 mark)***. This is because the ion has four bonding pairs on its central atom which will repel each other equally, giving bond angles of 109.5° ***(1 mark)***.

Module 3

Section 1 — The Periodic Table

1. The Periodic Table

Page 135 — Application Questions

Q1 a) 3 b) 4 c) 5

Q2 a) 6 b) 3 c) 1

Q3 a) $1s^2\ 2s^2\ 2p^6\ 3s^1$

b) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$

c) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$

d) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^3$

e) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^3\ 4s^2$

f) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^1\ 4s^2$

Page 135 — Fact Recall Questions

Q1 a) Mendeleev arranged the elements by atomic mass but left gaps where the next element didn't seem to fit so that he could keep elements with similar chemical properties in the same group.

b) In the modern periodic table the elements are arranged by increasing atomic number.

Q2 a) A period is a row in the periodic table.

b) A group is a column in the periodic table.

c) Periodicity means the repeating trends in the physical and chemical properties of the elements as you go across a period.

Q3 Elements in a group have similar chemical properties because they all have the same number of electrons in their outer shell.

2. First Ionisation Energy

Page 139 — Application Questions

Q1 a) $Cl_{(g)} \rightarrow Cl^+_{(g)} + e$

b) $Si_{(g)} \rightarrow Si^+_{(g)} + e$

Q2 a) Aluminium and sulfur are both in Period 3, so they both have the same number of electron shells, and a similar amount of shielding of the nuclear charge by the inner electron shells. Aluminium has 13 protons and sulfur has 16 protons. So the positive charge of the nucleus of sulfur is greater. This means electrons are pulled closer to the nucleus, making the atomic radius of sulfur smaller than the atomic radius of aluminium.

b) sodium/magnesium

Q3 The outer electron being removed is in the same energy level and the shielding is identical in the two atoms. But the silicon atom has one more proton than the aluminium atom so its nuclear charge is greater. This means that the attraction between the outer electron and the nucleus is greater in silicon, and it takes more energy to remove it.

Q4 a) Strontium would have a smaller atomic radius than rubidium. Strontium has a higher nuclear charge so there's a greater attraction between the electrons and the nucleus and so the electrons are pulled closer to the nucleus.

b) Bromine would have a higher first ionisation energy than selenium. The outer electron being removed is in the same energy level and the shielding is very similar in the two atoms. But the bromine atom has one more proton than the selenium atom so its nuclear charge is greater. This means that the attraction between the outer electron and the nucleus is greater in bromine, and it takes more energy to remove it.

Q5 The electron being removed is in the same energy level and the shielding is identical in the two atoms. However, the first ionisation energy of oxygen is lower than for nitrogen, despite oxygen having a higher nuclear charge. This is because the electron being removed from oxygen is in an orbital where there are two electrons. The repulsion between these two electrons means that it's easier to remove the electron than it would be if it was unpaired (like in nitrogen), so the first ionisation energy of oxygen is lower than that of nitrogen.

Q6 Boron's outer electron is in a 2p orbital rather than a 2s (like beryllium's), which means it has a higher energy and is located further from the nucleus. The 2p orbital also has additional shielding provided by the 2s electrons. These two factors override the effect of the increased nuclear charge of the boron atom, and result in the first ionisation energy of beryllium being higher than the first ionisation energy of boron.

Page 139 — Fact Recall Questions

Q1 The first ionisation energy is the energy needed to remove 1 mole of electrons from 1 mole of gaseous atoms.

Q2 The more protons there are, the more positively charged the nucleus is, the stronger the attraction for the electrons and the higher the ionisation energy.

Q3 The atomic radius and the shielding effect of inner electrons.

Q4 As you go down a group the number of electron shells increases. This means that the atomic radius get larger and there are more inner electron shells shielding the outer electron from the nucleus. As a result, the attraction between the nucleus and the outer electron is reduced so the outer electron is easier to lose and the first ionisation energy is lower.

Q5 a) There's a general increase in the first ionisation energy as you go across a period.

b) As you move across the period the amount of shielding remains roughly constant but the number of protons increases, so the strength of the nuclear attraction increases and the atomic radius decreases. As a result the electrons become more difficult to remove, increasing the first ionisation energy.

3. Successive Ionisation Energies

Page 141 — Application Questions

Q1 a) $B^{+}_{(g)} \rightarrow B^{2+}_{(g)} + e^{-}$

b) $Cl^{+}_{(g)} \rightarrow Cl^{2+}_{(g)} + e$

c) $Cl^{2+}_{(g)} \rightarrow Cl^{3+}_{(g)} + e^{-}$

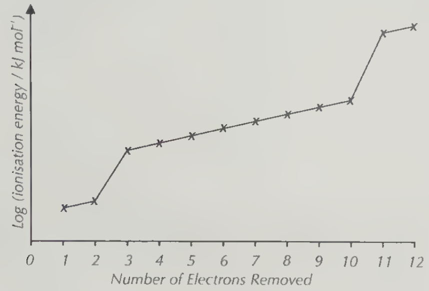
Q2 Fifth ionisation energy

Q3 a) Group 6

b) 2 electrons in the first shell and 6 electrons in the second shell.

c) Oxygen

Q4 a)



b) Within each shell, successive ionisation energies increase. This is because electrons are being removed from an increasingly positive ion — there's less repulsion amongst the remaining electrons, so they're held more strongly by the nucleus. The big jumps in ionisation energy happen when a new shell that's closer to the nucleus is broken into — the first shell has 2 electrons in it, the second shell has 8 electrons and the third shell has 2 electrons.

4. Giant Covalent Lattices

Page 143 — Fact Recall Questions

Q1 a) Diamond is a giant covalent lattice made up of carbon atoms. Each carbon atom is covalently bonded to four other carbon atoms and the atoms arrange themselves in a tetrahedral shape.

b) All the outer electrons are held in localised bonds.

Q2 Graphite is a giant covalent lattice made up of carbon atoms. Each carbon atom is covalently bonded to three other carbon atoms and the atoms arrange themselves in sheets of flat hexagons. The fourth outer electron of each carbon atom is delocalised between the sheets of hexagons. The sheets are bonded together by weak induced dipole-dipole forces.

Q3 a) Graphene is a giant covalent lattice made up of carbon atoms. Each carbon atom is covalently bonded to three other carbon atoms and the atoms arrange themselves in a single sheet of flat hexagons. Each sheet is one atom thick. The fourth outer electron of each carbon atom is delocalised above and below the sheet of hexagons.

b) The delocalised electrons in graphene are free to move quickly and freely above and below the sheet of carbon atoms, and so can carry an electric charge.

c) E.g. Graphene could be used in touchscreen technology/high-speed electronics/aircraft technology.

5. Metallic Bonding

Page 144 — Fact Recall Questions

Q1 Magnesium exists as a giant metallic lattice structure. The outermost electrons of magnesium atoms are delocalised — the electrons are free to move about the metal. This leaves positive metal ions, Mg^{2+}, which are attracted to the delocalised negative electrons. They form a lattice of closely packed positive ions in a sea of delocalised electrons.

Q2 metallic bonding

Q3 a) Copper shows metallic bonding. As there are no bonds holding specific ions together, the copper ions can slide over each other when the structure is pulled, so it can be drawn into a wire.

b) Since copper shows metallic bonding, there are delocalised electrons which can pass kinetic energy to each other, making copper a good thermal conductor.

6. Periodic Trends in Melting and Boiling Points

Page 146 — Application Questions

Q1 a) Lithium is a metal so it has strong metallic bonds holding all the atoms together. Nitrogen is a molecular substance with only induced dipole-dipole forces between the molecules. It takes much less energy to break induced dipole-dipole forces than metallic bonds, so the boiling point of lithium is much higher than the boiling point of nitrogen.

b) Beryllium and lithium are both metals so both have strong metallic bonds holding the atoms together. But a beryllium ion has a charge of 2+ so there are 2 delocalised electrons per ion, while a lithium ion only has a charge of 1+ and 1 delocalised electron per ion. As a result, beryllium ions have a greater charge density so the metallic bonds in beryllium are stronger and it has a higher boiling point.

Q2 a) Magnesium forms 2+ ions so there are two delocalised electrons for each ion. Sodium only forms 1+ ions so there is only one delocalised electron for each ion. Because magnesium contains more delocalised electrons than sodium, magnesium has a higher charge density so the metallic bonds in magnesium are stronger than the metallic bonds in sodium. As a result, more energy is required to break the bonds and the melting temperature of magnesium is higher.

b) Sulfur forms S_8 molecules while phosphorus forms P_4 molecules. Because sulfur molecules are larger than phosphorus molecules, the induced dipole-dipole forces which hold the molecules together are stronger. This means more heat energy is required to break the induced dipole-dipole forces and the melting point of sulfur is higher.

Q3 a) Silicon has a giant covalent lattice structure so has strong covalent bonds linking all its atoms together. Phosphorus is a molecular substance with induced dipole-dipole forces between its molecules. It takes much less energy to break induced dipole-dipole forces than covalent bonds so the melting point of phosphorus is much lower than the melting point of silicon.

b) chlorine / argon

Q4 Calcium would have a higher boiling point than potassium. The boiling point of metals increases across a period and calcium is after potassium in Period 4.

Page 146 — Fact Recall Questions

Q1 The melting and boiling points generally increase from lithium to carbon, but then decrease from carbon to neon.

Q2 boron, carbon

Q3 argon

7. Group 2 — The Alkaline Earth Metals

Pages 149-150 — Application Questions

Q1 a) $Ca_{(s)} + 2H_2O_{(l)} \rightarrow Ca(OH)_{2(aq)} + H_{2(g)}$

b) The oxidation state of calcium increases from 0 to +2.

c) The solution would fizz as bubbles of hydrogen gas are given off.

d) The reaction would be more vigorous/happen faster.

You know the reaction would be faster/more vigorous because reactivity increases down the group.

Q2 a) $2Sr_{(s)} + O_{2(g)} \rightarrow 2SrO_{(s)}$

b) Strontium oxide is a white solid.

c) $SrO_{(s)} + H_2O_{(l)} \rightarrow Sr^{2+}_{(aq)} + 2OH^-_{(aq)}$

d) pH 12 – 13

The solution is strongly alkaline due to the OH^- ions that are released when the strontium hydroxide dissolves in the water.

Q3 a) $Ca_{(s)} + 2HCl_{(aq)} \rightarrow CaCl_{2(aq)} + H_{2(g)}$

b) The oxidation state increases from 0 to +2.

c) The solution would fizz as bubbles of hydrogen gas are given off.

d) The reaction would be more vigorous if barium was used instead of calcium.

Page 150 — Fact Recall Questions

Q1 As you go down the group ionisation energy decreases. The lower the ionisation energy, the easier it is to lose electrons and the more reactive the element is. So reactivity increases down the group.

Q2 a) 2+

b) Group 2 elements have two electrons in their outer shell. When they lose these two electrons to form 2+ ions they end up with a full outer electron shell (the same as the noble gases). This is very stable so Group 2 elements usually form 2+ ions.

Q3 An increase in oxidation state from 0 to +2.

Q4 pH 12 – 13

Q5 Barium oxide

Q6 As you go down the group the reactivity of the elements with dilute acids increases.

Q7 E.g. calcium hydroxide is used in agriculture to neutralise acid soils. Magnesium hydroxide is used in some indigestion tablets as an antacid.

8. Group 7 — The Halogens

Page 155 — Application Questions

Q1 Bromine atoms have fewer electrons than iodine atoms. As a result the induced dipole-dipole forces in bromine are weaker than those in iodine. So less energy is required to break the intermolecular forces and the boiling point is lower.

Q2 a)

$$\begin{array}{lccccccc} & Cl_{2(aq)} & + & 2I^-_{(aq)} & \rightarrow & 2Cl^-_{(aq)} & + & I_{2(aq)} \\ \text{Oxidation no. of Cl:} & 0 & & & \rightarrow & -1 & & \\ \text{Oxidation no. of I:} & & & -1 & \rightarrow & & & 0 \end{array}$$

b) The solution turns from brown to a violet/pink colour.

Q3 Atoms of the other halogens have a larger atomic radius than fluorine atoms. This means their outer electrons are further from the nucleus and there are more electron shells shielding the outer electrons from the nucleus. So the nuclear attraction is less and it is more difficult for the other halogens to gain an electron. So they are less reactive than fluorine.

Q4 a) There are iodide ions in the unknown solution.

b) $Br_{2(aq)} + 2I^-_{(aq)} \rightarrow 2Br^-_{(aq)} + I_{2(aq)}$

Q5 A: iodide ions B: fluoride ions C: bromide ions

Page 155 — Fact Recall Questions

Q1 A diatomic molecule is a molecule consisting of two atoms.

Q2 The boiling points of the halogens increase down the group. This is due to the increasing strength of the induced dipole-dipole interactions as the size and relative mass of the atoms increases.

Q3 As you go down the group, the atomic radius increases so the outer electrons are further from the nucleus. The outer electrons are also shielded more from the attraction of the positive nucleus, because there are more inner electrons. This makes it harder for larger atoms to attract the electron needed to form an ion (despite the increased charge on the nucleus), so larger atoms are less reactive.

Q4 Bromide ions and iodide ions.

Q5 a) Pale yellow / green

b) Orange / red

c) Violet / pink

Q6 The silver nitrate test. Add dilute nitric acid to remove any ions that might interfere with the reaction. Then add silver nitrate and a precipitate may form. The colour of the precipitate identifies the halide (chloride gives a white precipitate, bromide gives a cream precipitate and iodide gives a yellow precipitate). If no precipitate forms it must be fluoride ions.

9. Disproportionation and Water Treatment

Page 158 — Application Questions

Q1 a) $I_{2(s)} + 2KOH_{(aq)} \rightarrow KIO_{(aq)} + KI_{(aq)} + H_2O_{(l)}$

b) The oxidation number of iodine increases from 0 in I_2 to +1 in KIO and decreases from 0 to –1 in KI. So iodine is simultaneously oxidised and reduced and it is a disproportionation reaction.

Q2 The oxidation state of O in H_2O_2 is –1. When H_2O is formed, the oxidation state of O decreases from –1 to –2. This is a reduction reaction. When O_2 is formed the oxidation state of O increases from –1 to 0. This is an oxidation reaction. So O is being simultaneously oxidised and reduced and it is a disproportionation reaction.

Q3 a) $HClO_{(aq)} + H_2O_{(l)} \rightarrow ClO^-_{(aq)} + H_3O^+_{(aq)}$

b) Chlorate(I) ions kill bacteria so adding them to water can make it safe to drink or swim in.

Page 158 — Fact Recall Questions

Q1 Disproportionation is when a single element is simultaneously oxidised and reduced during a reaction.

Q2 a) sodium chlorate(I), sodium chloride, water

b) $2NaOH_{(aq)} + Cl_{2(g)} \rightarrow NaClO_{(aq)} + NaCl_{(aq)} + H_2O_{(l)}$

Q3 When you mix chlorine with water, it undergoes disproportionation. It makes a mixture of hydrochloric acid and chloric(I) acid. The aqueous chloric(I) acid then ionises to make chlorate(I) ions.

Q4 a) Chlorine kills disease-causing microorganisms. It also prevents the growth of algae, eliminating bad tastes and smells, and removes discolouration caused by organic compounds.

b) Chlorine gas is very harmful if it's breathed in — it irritates the respiratory system. Liquid chlorine on the skin or eyes causes severe chemical burns. Accidents involving chlorine could be really serious, or fatal. Water contains a variety of organic compounds, e.g. from the decomposition of plants. Chlorine reacts with these compounds to form chlorinated hydrocarbons, e.g. chloromethane (CH_3Cl) — and many of these chlorinated hydrocarbons are carcinogenic (cancer-causing).

Q5 a) Ozone is a strong oxidising agent, so it is very good at killing microorganisms.

b) It's expensive to produce, and its half-life is short so treatment isn't permanent.

c) ultraviolet light

10. Tests for Ions

Page 161 — Application Questions

Q1 sulfate ions

Q2 a) His test could have produced false positives. If there were any carbonate ions or sulfite ions present then they would react with the barium nitrate solution to form a white precipitate. He didn't add a dilute strong acid first to remove any of these ions, so they could be present and interfere with the test.

b) He should add a dilute strong acid such as HCl or HNO_3 to the unknown solution to get rid of any unwanted carbonate or sulfite ions before adding the barium nitrate solution.

Page 161 — Fact Recall Questions

Q1 Carbonates, then sulfates, then halides.

Q2 a) E.g. hydrochloric acid / nitric acid

b) E.g. hydrochloric acid / nitric acid

c) nitric acid

Q3 blue

Exam-style Questions — pages 163-165

1 B ***(1 mark)***

2 A ***(1 mark)***

3 B ***(1 mark)***

4 a) (i) Arsenic, p-block ***(1 mark)***

(ii) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^3$ ***(1 mark)***

b) (i) $2Sr_{(s)} + O_{2(g)} \rightarrow 2SrO_{(s)}$ ***(1 mark)***

$2Ba_{(s)} + O_{2(g)} \rightarrow 2BaO_{(s)}$ ***(1 mark)***

(ii) Strontium and barium are in the same group of the periodic table so have similar electron configurations/have the same number of electrons in their outer shell ***(1 mark)***. This means they have similar chemical properties so they react with oxygen in similar ways ***(1 mark)***.

(iii) Barium will react more vigorously with oxygen than strontium will ***(1 mark)***. This is because barium has a lower ionisation energy ***(1 mark)***.

5 a) (i) $Ca_{(s)} + 2H_2O_{(l)} \rightarrow Ca(OH)_{2\,(aq)} + H_{2\,(g)}$ ***(1 mark)***.

(ii) A calcium atom has the electron configuration $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$.

The calcium ion in calcium hydroxide has the electron configuration $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$ ***(1 mark — both electron configurations must be correct)***.

(iii) The calcium would disappear/dissolve ***(1 mark)*** and the solution would fizz/bubbles would be produced ***(1 mark)***.

Make sure you describe what you actually see here. If you just say hydrogen gas is given off you won't get the mark because you can't actually see the hydrogen gas. What you can see is the bubbles that are produced.

(iv) pH 12-13 ***(1 mark)***.

b) (i) E.g Calcium hydroxide is used in agriculture to neutralise acidic soils ***(1 mark)***.

(ii) $H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)}$ ***(1 mark)***

6 a) (i) $Cl_{2(aq)} + 2Br^-_{(aq)} \rightarrow 2Cl^-_{(aq)} + Br_{2(aq)}$ ***(1 mark)***

(ii) Potassium bromide solution would give an orange/red colour ***(1 mark)***, whereas potassium iodide solution would give a violet/pink colour ***(1 mark)***.

b) (i) Add dilute nitric acid to the unknown solution, followed by silver nitrate ***(1 mark)***. A cream precipitate of AgBr will form if Br^- ions are present ***(1 mark)***.

(ii) $Ag^+_{(aq)} + Br^-_{(aq)} \rightarrow AgBr_{(s)}$ ***(1 mark)***

You know the AgBr has to be a solid because this is the precipitate that forms.

(iii) He could add ammonia solution and look at the solubility of the precipitate ***(1 mark)***. AgBr will dissolve in concentrated ammonia solution but not dilute ammonia solution ***(1 mark)***.

7 a) (i) diamond, graphite, graphene ***(1 mark)***

(ii) diamond ***(1 mark)***

(iii) Silicon has a giant covalent lattice structure ***(1 mark)***. Each silicon atom is covalently bonded to 4 other silicon atoms ***(1 mark)***.

b) (i) Carbon has one less proton in its nucleus than nitrogen does, so it has a lower nuclear charge ***(1 mark)*** and the attraction of the outer electrons to the nucleus is weaker ***(1 mark)***. This makes it less difficult to remove an electron so the ionisation energy of carbon is lower ***(1 mark)***.

(ii) ***5-6 marks:***

The answer correctly describes how the melting points of Period 2 elements change across the period and gives a full explanation for the changes, in terms of the structure and the bonding of the ions/atoms of each element. Giant metallic, giant covalent and simple molecular structures, the bonding within these structures and the strength of the forces that need to be overcome to melt the element are all explained. The answer has a clear and logical structure. The information given is relevant and detailed.

3-4 marks:

The answer correctly describes how the melting points of Period 2 elements change across the period and gives some explanation for the changes, in terms of the structure and the bonding of the ions/atoms of each element. Some aspects of the structure of giant metallic, giant covalent and simple molecular substances, the bonding within these structures and the strength of the forces that need to be overcome to melt the element are explained but the explanation may be incomplete.

The answer has some structure. Most of the information given is relevant and there is some detail involved.

1-2 marks:

The answer describes some of the changes in the melting points of Period 2 elements across the period. Little or no explanation is given for the changes.

The answer has no clear structure. The information given is basic and lacking in detail. It may not all be relevant.

0 marks:

No relevant information is given.

Here are some points your answer may include:

The melting points increase from lithium to carbon. The melting point decreases rapidly to nitrogen, oxygen, fluorine and neon (these have the lowest melting points of Period 2). The melting point increases from lithium to beryllium due to the increasing metallic bond strength from the increasing charge of the metal ions, the increasing number of delocalised electrons per ion and the decreasing ionic radius. These factors increase the strength of the metallic bonds in the giant metallic lattice. Boron and carbon have giant covalent lattice structures, so all of their atoms are bonded together by strong covalent bonds. A lot of energy is needed to break these bonds. Nitrogen, oxygen and fluorine have simple molecular structures. Only weak induced dipole-dipole forces between the molecules need to be overcome in order to melt the substance so they have low melting points.

Section 2 — Physical Chemistry

1. Enthalpy Changes

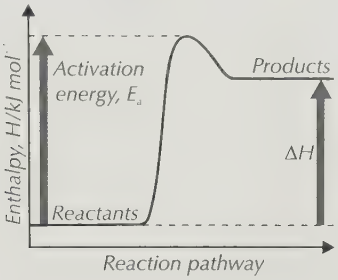
Page 167 — Fact Recall Questions

Q1 ΔH°

Q2 Standard enthalpy change of reaction, $\Delta_r H^\circ$, is the enthalpy change when a reaction occurs in the molar quantities shown in the chemical equation, under standard conditions with all reactants and products in their standard states.

Q3 Exothermic reactions give out energy, and endothermic reactions absorb energy. For exothermic reactions, the enthalpy change (ΔH) is negative. For endothermic reactions it is positive.

Q4 a)



b) (See part a) for arrow.) The activation energy, E_a, is the minimum amount of energy needed to break reactant bonds and start a chemical reaction.

2. Bond Enthalpies

Page 170 — Application Questions

Q1 a) Bonds broken = (1 × C=C) + (1 × H–H)
So total energy absorbed = 612 + 436
= 1048 kJ mol^{-1}.
Bonds formed = (2 × C–H) + (1 × C–C)
So total energy released = (2 × 413) + 347
= 1173 kJ mol^{-1}.
Enthalpy change of reaction
= total energy absorbed – total energy released
= 1048 – 1173 = **–125 kJ mol^{-1}**.

You can ignore any bonds that don't change when you're calculating the enthalpy change of a reaction.

b) Bonds broken = (1 × C–O) + (1 × H–Cl)
So total energy absorbed = 358 + 432
= 790 kJ mol^{-1}.
Bonds formed = (1 × C–Cl) + (1 × O–H)
So total energy released = 346 + 460
= 806 kJ mol^{-1}.
Enthalpy change of reaction
= total energy absorbed – total energy released
= 790 – 806 = **–16 kJ mol^{-1}**.

c) Bonds broken =
(2 × C–C) + (8 × C–H) + (5 × O=O)
So total energy absorbed =
(2 × 347) + (8 × 413) + (5 × 498) = 6488 kJ mol^{-1}.
Bonds formed = (6 × C=O) + (8 × O–H)
So total energy released = (6 × 805) + (8 × 460)
= 8510 kJ mol^{-1}.
Enthalpy change of reaction/combustion
= total energy absorbed – total energy released
= 6488 – 8510 = **–2022 kJ mol^{-1}**.

It really helps if you draw out a sketch for this question.

d) Bonds broken = (1 × C–Cl) + (1 × N–H)
Total energy absorbed = 346 + 391
= 737 kJ mol^{-1}
Bonds formed = (1 × C–N) + (1 × H–Cl)
Total energy released = 286 + 432
= 718 kJ mol^{-1}
Enthalpy change of reaction
= total energy absorbed – total energy released
= 737 – 718 = **+19 kJ mol^{-1}**

Q2 The balanced equation for the combustion of ethene is:
$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$.
Bonds broken =
(1 × C=C) + (4 × C–H) + (3 × O=O)
So total energy absorbed =
(1 × 612) + (4 × 413) + (3 × 498) = 3758 kJ mol^{-1}.
Bonds formed = (4 × C=O) + (4 × O–H)
So total energy released = (4 × 805) + (4 × 460)
= 5060 kJ mol^{-1}.
Enthalpy change of combustion
= total energy absorbed – total energy released
= 3758 – 5060 = **–1302 kJ mol^{-1}**.

Q3 The balanced equation for the formation of HCl is:
$H_2 + Cl_2 \rightarrow 2HCl$.
Bonds broken = (1 × H–H) + (1 × Cl–Cl)
So total energy absorbed = 436 + 243
= 679 kJ mol^{-1}.
Bonds formed = 2 × H–Cl
So total energy released = 2 × 432 = 864 kJ mol^{-1}.
Enthalpy change of reaction
= total energy absorbed – total energy released
= 679 – 864 = **–185 kJ mol^{-1}**.

Q4 Call the unknown bond enthalpy between N and O '*X*'.
Bonds broken = 2 × *X*
So total energy absorbed = 2*X* kJ mol^{-1}.
Bonds formed = (1 × N≡N) + (1 × O=O)
So total energy released = 945 + 498
= 1443 kJ mol^{-1}.
Enthalpy change of reaction = –181 kJ mol^{-1}
= total energy absorbed – total energy released.
So: –181= 2*X* – 1443
2*X* = –181 + 1443 = 1262
X = 1262 ÷ 2 = **+631 kJ mol^{-1}**.

Page 170 — Fact Recall Questions

Q1 endothermic

Q2 The energy required to make bonds.

Q3 Average bond enthalpy is the energy needed to break one mole of bonds in the gas phase, averaged over many different compounds.

Q4 Enthalpy change of reaction =
Total energy absorbed – Total energy released

3. Measuring Enthalpy Changes

Page 173 — Application Questions

Q1 $q = mc\Delta T = 220 \times 4.18 \times (301 - 298) = 2758.8$ J
$= 2.7588$ kJ

$$\Delta H = \frac{q}{n} = -\frac{2.7588 \text{ kJ}}{0.0500 \text{ mol}} = \mathbf{-55.2 \text{ kJ mol}^{-1}} \text{ (to 3 s.f.)}.$$

Don't forget — the enthalpy change must be negative because it's an exothermic reaction (you can tell because the temperature increased).

Q2 a) $q = mc\Delta T = 200 \times 4.18 \times 29.0 = 24\ 244$ J
$= 24.244$ kJ

$$n = \frac{\text{mass}}{M} = \frac{0.500 \text{ g}}{72 \text{ g mol}^{-1}} = 0.00694 \text{ moles of fuel}$$

$$\Delta H = \frac{q}{n} = -\frac{24.244 \text{ kJ}}{0.00694 \text{ mol}} = \mathbf{-3490 \text{ kJ mol}^{-1}} \text{ (to 3 s.f.)}.$$

b) E.g. some heat from the combustion will be transferred to the surroundings and not the water. / The combustion may not be complete combustion. / The combustion may not have taken place under standard conditions. / There could be inaccuracies due to the measuring equipment.

Q3 $q = mc\Delta T = 300 \times 4.18 \times 55.0 = 68\ 970 \text{ J} = 68.97$ kJ

$$\Delta_c H^{\ominus} \text{ octane} = -5512 \text{ kJ mol}^{-1} = \frac{q}{n}$$

$$n = \frac{q}{\Delta H} = \frac{68.97 \text{ kJ}}{5512 \text{ kJ mol}^{-1}} = 0.0125... \text{ mol.}$$

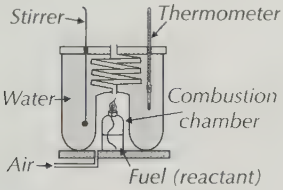
$$n = \frac{\text{mass}}{M}, \text{ so mass} = n \times M = 0.0125... \times 114$$

$= \mathbf{1.43\ g}$ of octane (to 3 s.f.).

Page 173 — Fact Recall Questions

Q1 The mass of reactant, the volume of the solution, and the initial and final temperature.

Q2 E.g.


Stirrer
Thermometer
Water
Combustion chamber
Air
Fuel (reactant)

Q3 q is the heat lost or gained during a reaction. It's measured in joules (J).

Q4 The reaction needs to be performed at a constant pressure of 100 kPa, with all reactants and products in their standard states.

Q5 Find the number of moles of that reactant that reacts in the balanced chemical equation, then calculate $\Delta_r H^{\ominus}$ using:

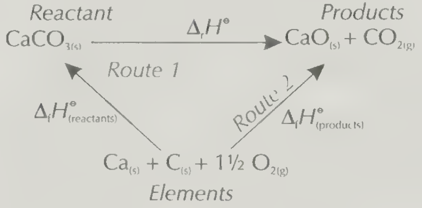
$$\Delta_r H^{\ominus} = \frac{q}{n} \times \text{number of moles reacting in balanced chemical equation}$$

4. Hess's Law

Page 176 — Application Questions

Q1 $\Delta_f H^{\ominus}_{\text{(reactants)}} = \Delta_f H^{\ominus}_{[\text{Mg}]} + (2 \times \Delta_f H^{\ominus}_{[\text{H}_2\text{O}]})$
$\Delta_f H^{\ominus}_{\text{(reactants)}} = 0 + (2 \times -286) = -572 \text{ kJ mol}^{-1}$.
$\Delta_f H^{\ominus}_{\text{(products)}} = \Delta_f H^{\ominus}_{[\text{Mg(OH)}_2]} + \Delta_f H^{\ominus}_{[\text{H}_2]}$
$\Delta_f H^{\ominus}_{\text{(products)}} = -925 + 0 = -925 \text{ kJ mol}^{-1}$.
Using Hess's Law: Route 1 = Route 2, so:
$\Delta_f H^{\ominus}_{\text{(reactants)}} + \Delta_r H^{\ominus} = \Delta_f H^{\ominus}_{\text{(products)}}$
$-572 + \Delta H_r^{\ominus} = -925$
$\Delta_r H^{\ominus} = -925 + 572 = \mathbf{-353 \text{ kJ mol}^{-1}}$.

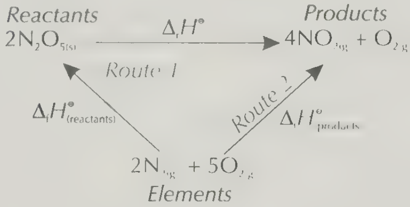
Q2 a) *First draw out a reaction scheme with an alternative reaction route that includes balanced equations for the formation of each compound:*


Reactant
$CaCO_{3(s)}$
$\Delta_r H^{\ominus}$
Products
$CaO_{(s)} + CO_{2(g)}$
Route 1
$\Delta_f H^{\ominus}_{\text{(reactants)}}$
Route 2
$\Delta_f H^{\ominus}_{\text{(products)}}$
$Ca_{(s)} + C_{(s)} + 1½\ O_{2(g)}$
Elements

$\Delta_f H^{\ominus}_{\text{(reactants)}} = \Delta_f H^{\ominus}_{[\text{CaCO}_3]} = -1207 \text{ kJ mol}^{-1}$.
$\Delta_f H^{\ominus}_{\text{(products)}} = \Delta_f H^{\ominus}_{[\text{CaO}]} + \Delta_f H^{\ominus}_{[\text{CO}_2]}$
$\Delta_f H^{\ominus}_{\text{(products)}} = -635 + -394 = -1029 \text{ kJ mol}^{-1}$.

Using Hess's Law: Route 1 = Route 2, so:
$\Delta_f H^{\ominus}_{\text{(reactants)}} + \Delta_r H^{\ominus} = \Delta_f H^{\ominus}_{\text{(products)}}$
$-1207 + \Delta_r H^{\ominus} = -1029$
$\Delta_r H^{\ominus} = -1029 + 1207 = \mathbf{+178 \text{ kJ mol}^{-1}}$.

b)


Reactants
$2N_2O_{5(s)}$
$\Delta_r H^{\ominus}$
Products
$4NO_{2(g)} + O_{2(g)}$
Route 1
$\Delta_f H^{\ominus}_{\text{(reactants)}}$
Route 2
$\Delta_f H^{\ominus}_{\text{products}}$
$2N_{2(g)} + 5O_{2(g)}$
Elements

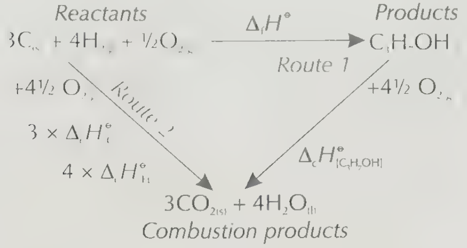
$\Delta_f H^{\ominus}_{\text{(reactants)}} = 2 \times \Delta_f H^{\ominus}_{[\text{N}_2\text{O}_5]}$
$\Delta_f H^{\ominus}_{\text{(reactants)}} = 2 \times -41 = -82 \text{ kJ mol}^{-1}$.
$\Delta_f H^{\ominus}_{\text{(products)}} = (4 \times \Delta_f H^{\ominus}_{[\text{NO}_2]}) + \Delta_f H^{\ominus}_{[\text{O}_2]}$
$\Delta_f H^{\ominus}_{\text{(products)}} = (4 \times 33) + 0 = 132 \text{ kJ mol}^{-1}$.

Remember that the enthalpy change of formation of O_2 is zero because it's an element.

Using Hess's Law: Route 1 = Route 2, so:
$\Delta_f H^{\ominus}_{\text{(reactants)}} + \Delta_r H^{\ominus} = \Delta_f H^{\ominus}_{\text{(products)}}$
$-82 + \Delta_r H^{\ominus} = 132$
$\Delta_r H^{\ominus} = 132 + 82 = \mathbf{+214 \text{ kJ mol}^{-1}}$.

Page 178 — Application Questions

Q1 a) *First draw out balanced reactions for the formation of the compound, and the combustion of the reactants and product:*


Reactants
Products
$\Delta_f H^\ominus$
$3C_{(s)} + 4H_{2(g)} + ½O_{2(g)}$
C_3H_7OH
Route 1
$+4½\ O_{2(g)}$
Route 2
$+4½\ O_{2(g)}$
$3 \times \Delta_c H^\ominus_{(C)}$
$4 \times \Delta_c H^\ominus_{(H_2)}$
$\Delta_c H^\ominus_{[C_3H_7OH]}$
$3CO_{2(s)} + 4H_2O_{(l)}$
Combustion products

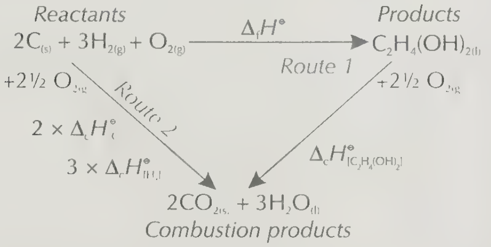
Using Hess's Law: Route 1 = Route 2, so:

$\Delta_f H^\ominus + \Delta_c H^\ominus_{[C_3H_7OH]} = (3 \times \Delta_c H^\ominus_{[C]}) + (4 \times \Delta_c H^\ominus_{[H_2]})$

$\Delta_f H^\ominus + (-2021) = (3 \times -394) + (4 \times -286)$

$\Delta_f H^\ominus = -1182 - 1144 + 2021 = \mathbf{-305\ kJ\ mol^{-1}}$.

b)


Reactants
Products
$\Delta_f H^\ominus$
$2C_{(s)} + 3H_{2(g)} + O_{2(g)}$
$C_2H_4(OH)_{2(l)}$
Route 1
$+2½\ O_{2(g)}$
Route 2
$+2½\ O_{2(g)}$
$2 \times \Delta_c H^\ominus_{(C)}$
$3 \times \Delta_c H^\ominus_{(H_2)}$
$\Delta_c H^\ominus_{[C_2H_4(OH)_2]}$
$2CO_{2(s)} + 3H_2O_{(l)}$
Combustion products

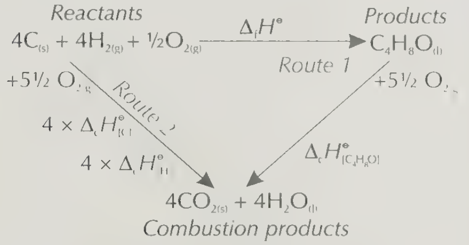
Using Hess's Law: Route 1 = Route 2, so:

$\Delta_f H^\ominus + \Delta_c H^\ominus_{[C_2H_4(OH)_2]} = (2 \times \Delta_c H^\ominus_{[C]}) + (3 \times \Delta_c H^\ominus_{[H_2]})$

$\Delta_f H^\ominus + (-1180) = (2 \times -394) + (3 \times -286)$

$\Delta_f H^\ominus = -788 - 858 + 1180 = \mathbf{-466\ kJ\ mol^{-1}}$.

c)


Reactants
Products
$\Delta_f H^\ominus$
$4C_{(s)} + 4H_{2(g)} + ½O_{2(g)}$
$C_4H_8O_{(l)}$
Route 1
$+5½\ O_{2(g)}$
Route 2
$+5½\ O_{2(g)}$
$4 \times \Delta_c H^\ominus_{(C)}$
$4 \times \Delta_c H^\ominus_{(H_2)}$
$\Delta_c H^\ominus_{[C_4H_8O]}$
$4CO_{2(s)} + 4H_2O_{(l)}$
Combustion products

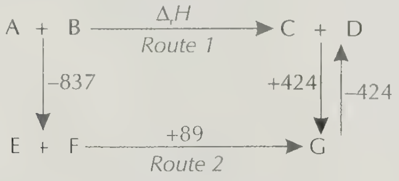
Using Hess's Law: Route 1 = Route 2, so:

$\Delta_f H^\ominus + \Delta_c H^\ominus_{[C_4H_8O]} = (4 \times \Delta_c H^\ominus_{[C]}) + (4 \times \Delta_c H^\ominus_{[H_2]})$

$\Delta_f H^\ominus + (-2442) = (4 \times -394) + (4 \times -286)$

$\Delta_f H^\ominus = -1576 - 1144 + 2442 = \mathbf{-278\ kJ\ mol^{-1}}$.

Q2 First label the reaction scheme with the known enthalpy changes, and the chosen routes:


A + B
$\Delta_r H$
Route 1
C + D
−837
+424
−424
E + F
+89
Route 2
G

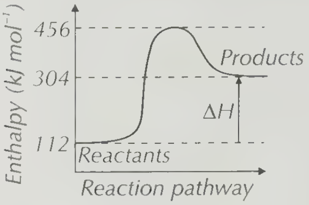
Using Hess's Law: Route 1 = Route 2, so:

$\Delta_r H = -837 + 89 + (-424) = \mathbf{-1172\ kJ\ mol^{-1}}$.

5. Reaction Rates

Page 181 — Application Questions

Q1



The reaction is endothermic (Δ*H* is positive) because the products have a higher enthalpy than the reactants.

Q2 B is the curve for the gas at a higher temperature because it is shifted over to the right, showing that more molecules have more energy.

Page 181 — Fact Recall Questions

Q1 The particles must collide in the right direction (facing each other the right way) and with at least a certain minimum amount of kinetic energy.

Q2 The minimum amount of kinetic energy that particles need to have in order to react when they collide.

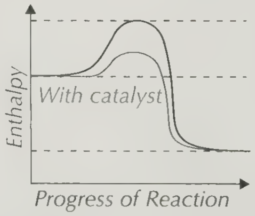
Q3 A small increase in temperature gives all molecules more energy, so a greater number of them have at least the minimum amount of energy to react when they collide. They will also collide more often because they will be moving about faster.

Q4 If you increase the concentration of reactants in a solution, the particles will be closer together in a given volume and so collide more often, increasing the reaction rate.

6. Catalysts

Page 184 — Application Question

Q1 a) E.g.



You can draw the line anywhere as long as the peak is lower than it was before and the shape of the graph stays the same.

b) Adding a catalyst would lower the activation energy for the reaction so that it would not need such a high temperature in order to take place. Being able to carry out the reaction at a lower temperature would save energy and money.

Page 184 — Fact Recall Questions

Q1 A substance that increases the rate of a reaction by providing an alternative reaction pathway with a lower activation energy. The catalyst is chemically unchanged at the end of the reaction.

Q2 Catalysts are used to speed up reactions in industrial processes that would be impossible or too slow to occur at practical temperatures and pressures. Using a catalyst means the temperature and pressure can be reduced, which saves energy and money.

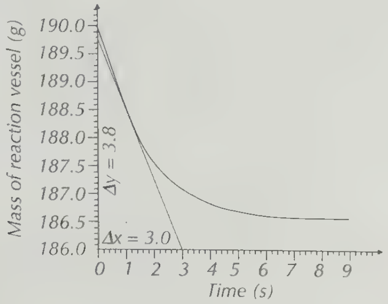
Q3 A catalyst increases the rate of a reaction by providing an alternative reaction pathway with a lower activation energy. This means that more of the molecules collide with energies above the activation energy, and so can react.

Q4 A homogeneous catalyst is in the same physical state as the reactants. A heterogeneous catalyst is in a different physical state from the reactants.

7. Calculating Reaction Rates

Page 187 — Application Question

Q1 a)

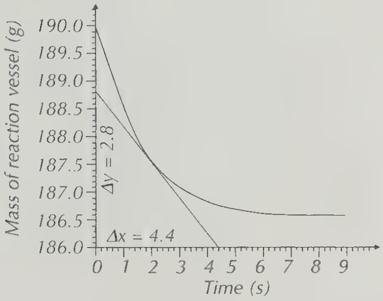


$$\text{gradient} = \frac{\Delta y}{\Delta x} = \frac{186.0 - 189.8}{3.0 - 0} = \frac{-3.8}{3.0} = -1.3$$

rate = 1.3 g s^{-1}

Drawing tangents accurately is tricky so there may be some variation between the answer you got and the 'official' answer. Don't worry though — in the exam, you'll usually be allowed a range of answers if you're asked to calculate a gradient. So for part a) allow yourself anything from 0.9 to 1.7.

b)

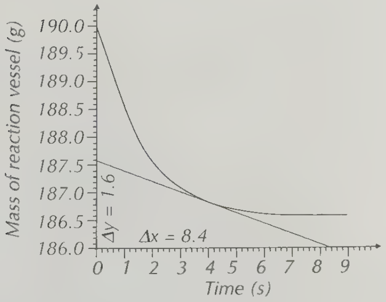


$$\text{gradient} = \frac{\Delta y}{\Delta x} = \frac{186.0 - 188.8}{4.4 - 0} = \frac{-2.8}{4.4} = -0.64$$

rate = 0.64 g s^{-1}

For part b) anything from 0.44 to 0.84 is OK.

c)



$$\text{gradient} = \frac{\Delta y}{\Delta x} = \frac{186.0 - 187.6}{8.4 - 0} = \frac{-1.6}{8.4} = -0.19$$

rate = 0.19 g s^{-1}

For part c) anything from 0.13 to 0.25 will do.

Page 187 — Fact Recall Questions

Q1 A reaction rate is the change in the amount of reactants or products per unit time.

Q2 E.g. g s^{-1} / cm^3 s^{-1}

Q3 E.g. by measuring the volume of gas produced / by measuring the change in mass.

Q4 a) Measure the mass of a reaction vessel at regular time points as a reaction progresses.
Plot mass against time to produce a mass-time graph.

b) Measure the gradient of the graph at that particular time.
The gradient is the rate of reaction.

8. Reversible Reactions

Page 192 — Application Questions

Q1 a) Increasing the concentration of A will shift the equilibrium to the right (favouring the forwards reaction) in order to get rid of the excess A.

b) There are 3 moles of gas on the left and only 2 moles of gas on the right. Increasing the pressure will shift the equilibrium to the right (favouring the forwards reaction) in order to reduce the number of moles of gas to reduce the pressure again.

c) The forwards reaction is exothermic, so the backwards reaction must be endothermic. Increasing the temperature will shift the equilibrium to the left (favouring the endothermic backwards reaction) in order to remove the extra heat energy.

d) The reaction should ideally be performed with a high concentration of A and B, at a high pressure and low temperature.

Q2 There are the same number of moles of gas on either side of the reaction. Increasing the pressure favours the reaction producing the fewest moles of gas, but since both reactions are equal in this respect, increasing the pressure will not shift the position of equilibrium.

Page 192 — Fact Recall Questions

Q1 The concentrations of reactants and products are constant, and the forwards reaction and the backwards reaction are going at the same rate.

Q2 If there's a change in concentration, pressure or temperature, the equilibrium will move to help counteract the change.

Q3 The addition of a catalyst has no effect on the position of equilibrium in a reversible reaction.

Q4 A low temperature would reduce the rate of reaction. This means that although you'd get a high yield it would take so long that it wouldn't be worth it.

9. The Equilibrium Constant

Page 194 — Application Questions

Q1 $K_c = \frac{[C_2H_5OH]}{[C_2H_4][H_2O]}$

Q2 a) $K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$

b) $K_c = \frac{[SO_3]^2}{[SO_2]^5[O_2]} = \frac{0.360^2}{(0.250)^2(0.180)} = 11.5$

$K_c = \frac{(\text{mol dm}^{-3})^2}{(\text{mol dm}^{-3})^2(\text{mol dm}^{-3})} = \frac{1}{(\text{mol dm}^{-3})}$

K_c = **11.5 mol^{-1} dm^3**

Page 194 — Fact Recall Questions

Q1 $K_c = \frac{[D]^d[E]^e}{[A]^a[B]^b}$

Q2 K_c changes with temperature. So a given value of K_c is only true at the temperature it was measured at.

Q3 As the temperature increases, the value of K_c increases, so the equilibrium must have shifted to the right.

Exam-style Questions — pages 197-201

1 a) B ***(1 mark)***

Since the y-axis is 'number of molecules', the maximum of the distribution corresponds to the most likely energy of the molecules in the distribution.

b) C ***(1 mark)***

At higher temperatures, Boltzmann distributions are pushed over to the right, but keep the same area under the distribution.

2 A ***(1 mark)***

The independent variable is the variable which you deliberately change during the experiment.

3 a) In a reversible reaction, dynamic equilibrium is reached when the concentrations of reactants and products are constant ***(1 mark)***, and the forwards reaction and the backwards reaction are going at the same rate ***(1 mark)***.

b) The higher the pressure, the faster the reaction rate ***(1 mark)***. A high pressure also favours the forwards reaction, which produces fewer moles of gas, so the higher the pressure, the greater the yield of ethanol ***(1 mark)***. However, high pressures are very expensive / can produce side reactions / require strong and expensive equipment, so the pressure used is limited by these factors ***(1 mark)***.

c) Reducing the amount of H_2O will shift the position of equilibrium to the left ***(1 mark)*** in order to increase the amount of H_2O present ***(1 mark)***. This shift will reduce the maximum yield of ethanol from the forwards reaction ***(1 mark)***.

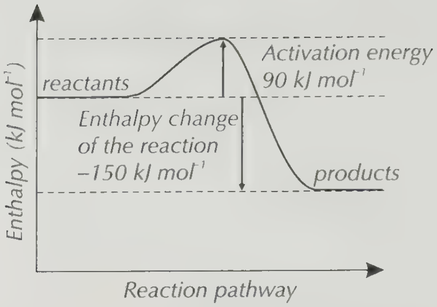
d) $K_c = \frac{[C_2H_5OH]}{[C_2H_4][H_2O]} = \frac{2.70}{0.400 \times 0.400}$

= **16.9 mol^{-1} dm^3**

(2 marks for correct answer, otherwise 1 mark for correct equilibrium constant equation.)

4 a) (i) The minimum amount of kinetic energy ***(1 mark)*** that particles need to have in order to react when they collide ***(1 mark)***.

(ii)


Enthalpy (kJ mol^{-1})
reactants
Activation energy 90 kJ mol^{-1}
Enthalpy change of the reaction −150 kJ mol^{-1}
products
Reaction pathway

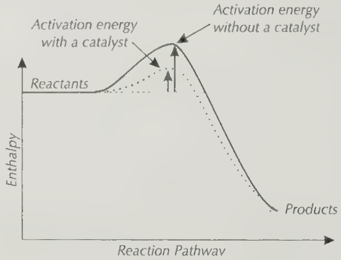
(1 mark for correctly labelled axes, 1 mark for products lower than reactants, 1 mark for correctly labelled activation energy, 1 mark for correctly labelled enthalpy change of reaction.)

b) Heating the reactants gives the molecules more energy ***(1 mark)***. This means that more molecules will have an energy higher than the activation energy ***(1 mark)***, so more collisions between molecules will result in reaction, increasing the reaction rate ***(1 mark)***.

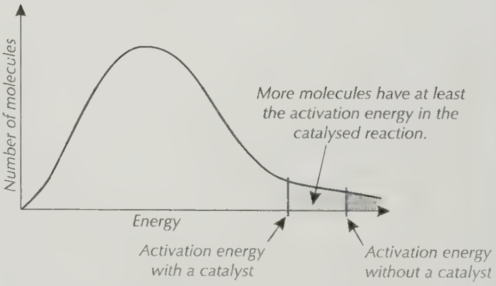
c) Lowering the pressure will reduce the rate of reaction ***(1 mark)***. This is because there will be fewer gas molecules in a given volume/the concentration will be reduced/the molecules will be further apart ***(1 mark)***, so there will be fewer collisions between molecules that result in reaction ***(1 mark)***.

d) (i) A catalyst is a substance that increases the rate of a reaction without being changed or used up by the reaction ***(1 mark)***.

(ii)


Activation energy with a catalyst
Activation energy without a catalyst
Reactants
Enthalpy
Products
Reaction Pathwav

(1 mark for diagram with correctly labelled activation energy)

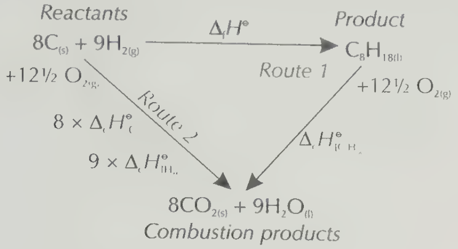


(1 mark for diagram with correctly labelled axes)

A catalyst increases the rate of a reaction by providing an alternative reaction pathway ***(1 mark)*** with a lower activation energy ***(1 mark)***. With a catalyst present, the molecules still have the same amount of energy ***(1 mark)***, so the Boltzmann distribution curve is unchanged. But because the catalyst lowers the activation energy, more of the molecules have energies above this threshold and are able to react ***(1 mark)***.

5 a) $C_8H_{18(l)} + 12½O_{2(g)} \rightarrow 8CO_{2(g)} + 9H_2O_{(l)}$ ***(1 mark)***

b) (i)



Using Hess's Law: Route 1 = Route 2, so:

$\Delta_f H^\ominus + \Delta_c H^\ominus_{[C_8H_{18}]} = (8 \times \Delta_c H^\ominus_{[C]}) + (9 \times \Delta_c H^\ominus_{[H_2]})$

$\Delta_f H^\ominus + (-5470) = (8 \times -394) + (9 \times -286)$

$\Delta_f H^\ominus = -3152 - 2574 + 5470 =$ **-256 kJ mol^{-1}**.

(3 marks for correct answer, otherwise 1 mark for correct equation using Hess's Law and 1 mark for correct molar quantities. Allow 1 mark only for an answer of +256 kJ mol⁻¹.)

(ii) Exothermic ***(1 mark)***. The enthalpy change for the formation of octane is negative ***(1 mark)***.

c) (i) $q = mc\Delta T = 325 \times 4.18 \times 13.0 = 17\,660.5$ J
$= 17.6605$ kJ

$$n = \frac{\text{mass}}{M} = \frac{0.4503 \text{ g}}{114 \text{ g mol}^{-1}} = 0.00395 \text{ moles of fuel}$$

$$\Delta H = \frac{q}{n} = -\frac{17.6605 \text{ kJ}}{0.00395 \text{ mol}} = \mathbf{-4470 \text{ kJ mol}^{-1}} \text{ (3 s.f.)}.$$

(2 marks for correct answer, otherwise 1 mark for correct value of heat gained (q).)

(ii) Any two from e.g. some heat from the combustion will be transferred to the surroundings and not the water. / The combustion may not be complete combustion. / The combustion may not have taken place under standard conditions. / There could be inaccuracies due to the measuring equipment. ***(1 mark each up to a maximum of 2 marks)***.

6 a) (i) Standard enthalpy of combustion, $\Delta_c H^\ominus$, is the enthalpy change when 1 mole of a substance ***(1 mark)*** is completely burned in oxygen ***(1 mark)*** under standard conditions with all reactants and products in their standard states ***(1 mark)***.

(ii) The balanced equation for the combustion of but-1-ene is: $C_4H_8 + 6O_2 \rightarrow 4CO_2 + 4H_2O$.

Bonds broken =
(1 × C=C) + (2 × C–C) + (8 × C–H) + (6 × O=O)
So total energy absorbed =
(1 × 612) + (2 × 347) + (8 × 413) + (6 × 498)
= 7598 kJ mol^{-1}.
Bonds formed = (8 × C=O) + (8 × O–H)
So total energy released = (8 × 805) + (8 × 460)
= 10 120 kJ mol^{-1}.
Enthalpy change of combustion
= total energy absorbed – total energy released
= 7598 – 10 120 = **–2522 kJ mol^{-1}**.

(3 marks for correct answer, otherwise 1 mark for 'total energy absorbed – total energy released', and 1 mark for correct value for either energy released or energy absorbed. Allow 1 mark only for an answer of +2522 kJ mol⁻¹).

(iii) Some of the average bond enthalpies are average values for the bonds in many different compounds, so they are not accurate for the specific molecules involved in this combustion ***(1 mark)***.

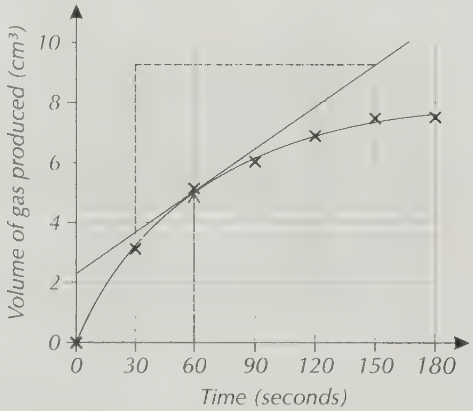
b) (i) $q = mc\Delta T = 200 \times 4.18 \times 32.8 = 27400$ J
= **27.4 kJ** (to 3 s.f.)
(2 marks for correct answer, otherwise 1 mark for correct working.)

(ii) $\Delta_c H^\ominus = q \div n = 27.4 \div 0.0215$
= **–1270 kJ mol^{-1}** (to 3 s.f.)
(1 marks for correct answer, 1 mark for minus sign)

(iii) When the reaction happens, reactant bonds are broken and product bonds are formed ***(1 mark)***. The total energy needed to break the alkene bonds is less than the energy released when the product bonds are formed ***(1 mark)*** so the reaction is exothermic.

7 a) A gas syringe should be used to collect the hydrogen gas escaping from the reaction vessel ***(1 mark)***. A stop clock or timer should be used to time the reaction so that measurements of gas volume can be taken at certain time intervals ***(1 mark)***.

b)



(1 mark for a correctly drawn tangent.)

Rate of reaction = gradient of tangent at 1 minute.
gradient = change in y ÷ change in x
e.g. = (9.2 – 3.6) ÷ (150 – 30)
= **0.047 cm^3 s^{-1}** (to 2 s.f.)

(1 mark for correct answer ±0.01 cm³ s⁻¹.)

Different people will draw slightly different tangents and pick different spots on the tangent so there's a margin of error in this answer. 0.047 (± 0.01) cm^3 s^{-1} means any answer between 0.037 cm^3 s^{-1} and 0.057 cm^3 s^{-1} is worth the mark.

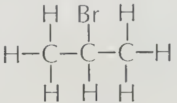
Module 4

Section 1 — Basic Concepts and Hydrocarbons

2. Formulas

Pages 205-206 — Application Questions

Q1



$$\begin{array}{ccccccc} & & \mathrm{H} & \mathrm{Br} & \mathrm{H} & & \\ & & | & | & | & & \\ \mathrm{H} & - & \mathrm{C} - & \mathrm{C} - & \mathrm{C} & - & \mathrm{H} \\ & & | & | & | & & \\ & & \mathrm{H} & \mathrm{H} & \mathrm{H} & & \end{array}$$

It doesn't matter if you draw the bromine atom above or below the carbon atom — it means the same thing.

Q2 C_8H_{18}

Q3 a) CH_2

b) C_4H_7Br

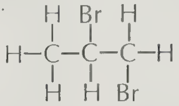
c) $C_9H_{17}Cl_3$

Q4 a) C_4H_8

b) Heptene contains 14 H atoms.

Q5 a) $C_3H_6Br_2$

b) E.g.



$$\begin{array}{ccccccc} & & \mathrm{H} & \mathrm{Br} & \mathrm{H} & & \\ & & | & | & | & & \\ \mathrm{H} & - & \mathrm{C} - & \mathrm{C} - & \mathrm{C} & - & \mathrm{H} \\ & & | & | & | & & \\ & & \mathrm{H} & \mathrm{H} & \mathrm{Br} & & \end{array}$$

c) $C_3H_6Br_2$

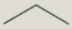
For this molecule the empirical formula is the same as the molecular formula because you can't cancel the atoms down and still have whole numbers.

Q6 a) C_5H_{10}

b) $CH_3CH_2CH_2CHCH_2$

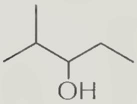
c) CH_2

Q7 a)

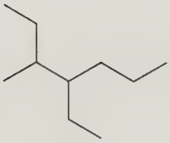


Skeletal formulas have a carbon atom at each end and at each junction.

b)



c)



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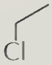


Q8 a) $CH_3CH(CH_3)CH(CH_3)CH_2CH_2CH_3$

b) $CH_3CH_2C(CH_2)CH_2CH_2CH_3$

c) $CH_3CH_2CClCHCH_2CH_3$

d) $CH_3CHBrCH(OH)CH_2CHCH_2$

Page 206 — Fact Recall Questions

Q1 A general formula is used to represent a homologous series.

Q2 A homologous series is a family of organic compounds which have the same general formula and similar chemical properties.

Q3 A displayed formula shows how all the atoms are arranged, and all the bonds between them.

Q4 The carbon and hydrogen atoms of the main carbon chain aren't shown.

3. Carbon Skeletons

Page 207 — Application Questions

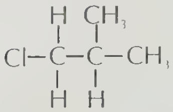
Q1 C_3H_7

Q2 unsaturated

4. Structural Isomers

Page 210 — Application Questions

Q1 E.g.

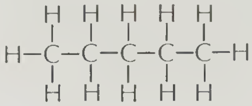


$$\begin{array}{ccccc} & \mathrm{H} & \mathrm{CH_3} & & \\ & | & | & & \\ \mathrm{Cl} - & \mathrm{C} - & \mathrm{C} & - & \mathrm{CH_3} \\ & | & | & & \\ & \mathrm{H} & \mathrm{H} & & \end{array}$$

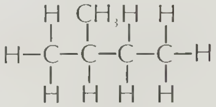
You could draw the chlorine atom attached to any other carbon atom apart from the one it was on originally.

Q2 There are three chain isomers of C_5H_{12}.

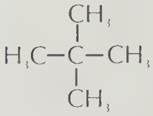
E.g.



$$\begin{array}{ccccccccc} & & \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{H} & & \\ & & | & | & | & | & | & & \\ \mathrm{H} & - & \mathrm{C} - & \mathrm{C} - & \mathrm{C} - & \mathrm{C} - & \mathrm{C} & - & \mathrm{H} \\ & & | & | & | & | & | & & \\ & & \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{H} & & \end{array}$$

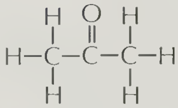


$$\begin{array}{cccccccc} & & \mathrm{H} & \mathrm{CH_3} & \mathrm{H} & \mathrm{H} & & \\ & & | & | & | & | & & \\ \mathrm{H} & - & \mathrm{C} - & \mathrm{C} - & \mathrm{C} - & \mathrm{C} & - & \mathrm{H} \\ & & | & | & | & | & & \\ & & \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{H} & & \end{array}$$



$$\begin{array}{ccccc} & & \mathrm{CH_3} & & \\ & & | & & \\ \mathrm{H_3C} & - & \mathrm{C} & - & \mathrm{CH_3} \\ & & | & & \\ & & \mathrm{CH_3} & & \end{array}$$

Q3



$$\begin{array}{ccccccc} & & \mathrm{H} & \mathrm{O} & \mathrm{H} & & \\ & & | & \| & | & & \\ \mathrm{H} & - & \mathrm{C} - & \mathrm{C} - & \mathrm{C} & - & \mathrm{H} \\ & & | & & | & & \\ & & \mathrm{H} & & \mathrm{H} & & \end{array}$$

Q4 a) A and B

b) chain isomerism

Page 210 — Fact Recall Questions

Q1 Isomers are molecules with the same molecular formula but a different arrangement of atoms.

Q2 Structural isomers have the same molecular formula but different structural formulas.

5. Alkanes and Nomenclature

Page 214 — Application Questions

Q1 a) butane

b) ethane

c) methane

d) nonane

e) heptane

f) decane

Q2 a) 3-methylpentane

b) 3-ethyl-3-methylpentane

c) 3,3-diethylhexane

d) 3,3-diethyl-2-methylhexane

Page 214 — Fact Recall Questions

Q1 An alkane is a saturated hydrocarbon containing only C–C and C–H bonds.

Q2 C_nH_{2n+2}

Q3 hex-

Q4 ethyl-

Q5 di-

6. Properties of Alkanes

Page 219 — Application Questions

Q1 a) Octane molecules are larger than propane molecules, so there is more surface contact between the octane molecules than the propane molecules. As a result the induced dipole-dipole interactions between octane molecules are stronger than those between propane molecules. So more energy is required to break the forces and the boiling point is higher.

In questions like this, make sure you give your answer as a comparison. If you just say octane molecules are big so it has a high boiling point you won't get the marks. You have to say that octane molecules are bigger than propane molecules so octane has a higher boiling point than propane.

b) Complete combustion:
$2C_8H_{18} + 25O_2 \rightarrow 16CO_2 + 18H_2O$ /
$C_8H_{18} + 12\frac{1}{2}O_2 \rightarrow 8CO_2 + 9H_2O$
Incomplete combustion:
$2C_8H_{18} + 17O_2 \rightarrow 16CO + 18H_2O$ /
$C_8H_{18} + 8\frac{1}{2}O_2 \rightarrow 8CO + 9H_2O$

Q2 2,2-dimethylpropane is branched, so the molecules don't pack together closely and there is less surface contact between molecules than in pentane, which is a straight-chain molecule. As a result there are more induced dipole-dipole interactions between molecules of pentane than between 2,2-dimethylpropane molecules and so more energy is required to break them. So pentane has the higher boiling point.

Q3 First write out the combustion equation using the values provided: $20X + 130O_2 \rightarrow 80CO_2 + ?H_2O$
Divide through by 20 so that there is only one mole of X on the left-hand side of the equation:
$X + 6\frac{1}{2}O_2 \rightarrow 4CO_2 + nH_2O$

It's OK to have ½ values in your reaction equation.

6½ moles of oxygen react to form 4 moles of carbon dioxide and *n* moles of water. So any oxygen atoms that don't end up in CO_2 must be in H_2O.
This means that $n = (6\frac{1}{2} \times 2) - (4 \times 2) = 5$
So the reaction equation is $X + 6\frac{1}{2}O_2 \rightarrow 4CO_2 + 5H_2O$.
All the carbon atoms from X end up in carbon dioxide, and all the hydrogen atoms from X end up in water, so the number of carbon atoms in X is 4 and the number of hydrogen atoms in X is 10.
The molecular formula of X is $\mathbf{C_4H_{10}}$.

Page 219 — Fact Recall Questions

Q1 The atoms or groups form tetrahedral shapes around each carbon.

Q2 σ-bonds form when atomic orbitals on neighbouring atoms overlap to form a new orbital directly between the bonded atoms.

Q3 E.g. the length of the carbon–carbon chain and the amount of branching in the molecule.

Q4 The products of complete combustion are carbon dioxide and water. The products of incomplete combustion are carbon monoxide and water (and sometimes particulate carbon and carbon dioxide).

Q5 Carbon monoxide binds to haemoglobin in the blood. This prevents the haemoglobin binding to oxygen. As a result, less oxygen can be transported around the body and symptoms of oxygen deprivation occur.

7. Bond Fission

Page 220 — Fact Recall Questions

Q1 The breaking of a covalent bond.

Q2 a) Heterolytic fission and homolytic fission.

b) In heterolytic fission the bond breaks unevenly, and one of the bonded atoms ends up with both of the bonding electrons. Two different substances are formed — a positively charged cation and a negatively charged anion. In homolytic fission, the bond breaks evenly, with each of the bonded atoms receiving one of the bonding electrons. Two electrically uncharged radicals are formed.

Q3 A radical is a particle with an unpaired electron.

Q4 You use a dot.

Q5 The movement of a pair of electrons.

8. Substitution Reactions

Page 222 — Application Questions

Q1 a) Initiation, propagation and termination.

b) Initiation: $Br_2 \rightarrow 2Br\cdot$
Propagation: $Br\cdot + CH_4 \rightarrow CH_3\cdot + HBr$
$CH_3\cdot + Br_2 \rightarrow CH_3Br + Br\cdot$
Termination: E.g. $CH_3\cdot + Br\cdot \rightarrow CH_3Br$ /
$CH_3\cdot + CH_3\cdot \rightarrow C_2H_6$

c) E.g. CH_2Br_2 / $CHBr_3$ / CBr_4

Q2 a) radical substitution

b) Initiation: UV light provides enough energy to split the Cl–Cl bond (homolytic fission), this produces two radicals.
$Cl_2 \rightarrow 2Cl\cdot$
Propagation: radicals are created and used up in a chain reaction.
E.g. $Cl\cdot + C_2H_6 \rightarrow C_2H_5\cdot + HCl$
E.g. $C_2H_5\cdot + Cl_2 \rightarrow C_2H_5Cl + Cl\cdot$
Termination: the radicals are mopped up — two radicals react together to form a stable molecule.
E.g. $C_2H_5\cdot + Cl\cdot \rightarrow C_2H_5Cl$ / $C_2H_5\cdot + C_2H_5\cdot \rightarrow C_4H_{10}$

c) Make sure the ethane is in excess.

Page 222 — Fact Recall Questions

Q1 $Cl_2 + CH_4 \rightarrow CH_3Cl + HCl$

Q2 homolytic fission

Q3 Some or all of the hydrogen atoms found on haloalkane molecules can be swapped for halogen atoms, creating multi-substituted products like CH_2Cl_2, $CHCl_3$ and CCl_4. For alkanes with longer carbon chains than methane. substitution can also happen at any point on a carbon chain, which can lead to a mixture of isomers such as 1-chloropropane and 2-chloropropane.

9. Alkenes and their Properties

Page 226 — Application Questions

Q1 a) propene
b) but-2-ene
c) hexa-1,3-diene / 1,3-hexadiene
d) methylpropene

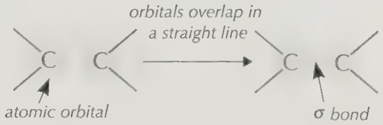
Q2 Propene is an alkene so it contains a double bond. Because there are two electron pairs in the bond the C=C double bond has a really high electron density. Plus, the π bond sticks out above and below the rest of the molecule. These two factors mean that propene is susceptible to attack by electrophiles. Propane doesn't contain a double bond so isn't susceptible to attack by electrophiles. So propene is more reactive.

Q3 Double bonds are formed from a sigma bond and a pi bond. Single bonds are just sigma bonds. The pi bond is weaker than the sigma bond so the double bond is not twice as strong as a single bond.

Page 226 — Fact Recall Questions

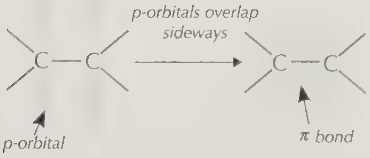
Q1 C_nH_{2n}

Q2 a)



This is how you need to draw your diagram in the exam (though it doesn't have to be coloured in). Make sure you label the atomic orbitals and the sigma bond and make sure you say how the orbitals are overlapping. Otherwise you might lose out on valuable marks.

b)



Q3 electrophiles

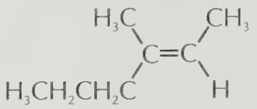
Q4 a) Trigonal planar means that all of the atoms lie in the same plane and are at the corners of an imaginary equilateral triangle with bond angles of 120° between them, like the atoms attached to a double-bonded carbon atom.
b) The atoms attached to each carbon in the C=C double bond of alkenes have a trigonal planar shape.

10. Stereoisomers

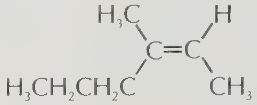
Page 229 — Application Questions

Q1 a) (i) *Z*-isomer
(ii) *E*-isomer
b) (i) *cis*-isomer
(ii) *trans*-isomer

Q2



E-isomer



Z-isomer

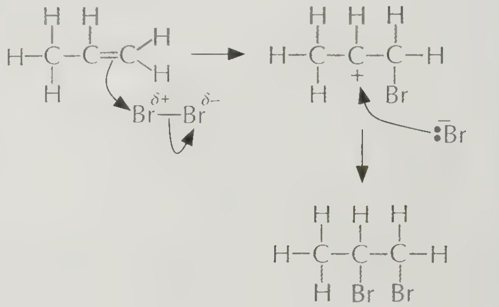
The highest priority group on carbon-2 is $-CH_3$, and on carbon-3 it's $-CH_2CH_2CH_3$.

11. Reactions of Alkenes

Page 235 — Application Questions

Q1 pentane

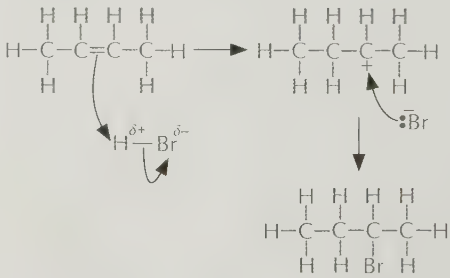
Q2 a) $CH_3CHCH_2 + Br_2 \rightarrow CH_3CHBrCH_2Br$
b) electrophilic addition



If you're asked to name and outline a mechanism, make sure you do just that. It's really easy to forget the name and dive straight in to the mechanism — but don't forget or you'll lose a valuable mark in the exam.

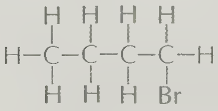
c) It doesn't contain a C=C double bond / it is saturated.

Q3

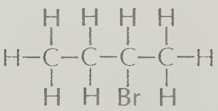


It doesn't matter which carbon you add the bromine to as you'll always end up with the same product (2-bromobutane).

Q4 a)



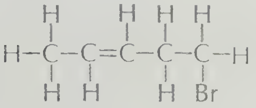
1-bromobutane

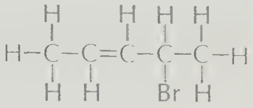


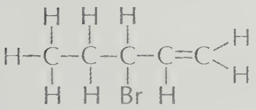
2-bromobutane

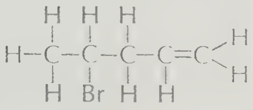
b) The major product is 2-bromobutane. This is because it forms via the formation of a secondary carbocation, which is more stable and so more likely to form than the primary carbocation that is formed in the formation of 1-bromobutane.

Q5 If only one HBr adds onto the molecule you could get any of these products:

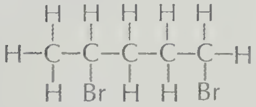


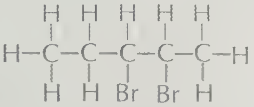


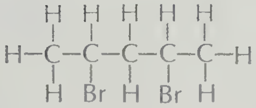


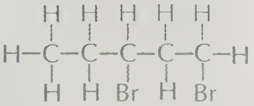


If two HBr add onto the molecule you could get any of these molecules:









Give yourself a pat on the back if you managed to get all of these molecules.

Page 235 — Fact Recall Questions

Q1 An electrophile is an electron pair acceptor.

Q2 Any two from: e.g. NO_2^+ / H^+ / HBr / Br_2.

Q3 hydrogen bromide

Q4 carbon-carbon double bonds / unsaturation / alkenes

Q5

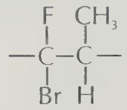
$$H_2C{=}CH_{2(g)} + H_2O_{(g)} \xrightleftharpoons[\substack{300\ ^\circ C\\ 60\ atm}]{H_3PO_4} CH_3CH_2OH_{(g)}$$

Q6 That the major product from the addition of a hydrogen halide to an unsymmetrical alkene is the one where hydrogen adds to the carbon with the most hydrogens already attached / the one that forms as a result of the formation of the most stable carbocation in the reaction mechanism.

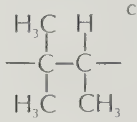
12. Addition Polymers

Page 237 — Application Questions

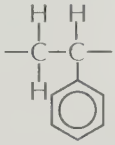
Q1 a)



b)

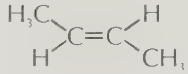


c)

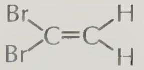


If you're asked to draw more than one repeating unit in the exam, make sure you draw them all linked together. You won't get the marks if you draw them separately.

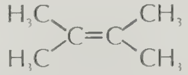
Q2 a)



b)



c)



Page 239 — Fact Recall Questions

Q1 addition polymers

Q2 The double bond of the alkene opens up and the alkenes join together to form a polymer.

Q3 a) It means they won't react when they are being used (e.g. food doesn't react with PTFE coating on pans, plastic windows don't rot etc.).
b) Because they are unreactive, most plastics are non-biodegradable, so disposing of them is a problem.

Q4 E.g. by melting and remoulding / by cracking into monomers which can be used as an organic feedstock to make more plastic or other chemicals.

Q5 a) HCl
b) By passing the waste gases through a scrubber which can neutralise the HCl by allowing it to react with a base.

Q6 E.g. renewable raw materials aren't going to run out like oil will / if the polymer is plant-based the CO_2 released as it decomposes is the same CO_2 absorbed by the plant when it grew, so it is more carbon-neutral than using non-renewable raw materials / over their lifetime some plant-based polymers save energy compared to oil-based plastics.

Q7 E.g. they require specific conditions to decompose so can't just be placed in a landfill — they still have to be separated from other waste / they are more expensive than oil-based equivalents.

Exam-style Questions — pages 241-243

Q1 B ***(1 mark)***

Q2 A ***(1 mark)***

Q3 a) (i) Radicals are particles that have an unpaired electron ***(1 mark)***.

(ii) homolytic fission ***(1 mark)***

b) (i) $CH_3CH_3 + Br_2 \rightarrow CH_3CH_2Br + HBr$ ***(1 mark)***

(ii) Initiation: $Br_2 \rightarrow 2Br\cdot$ ***(1 mark)***

Propagation: $Br\cdot + CH_3CH_3 \rightarrow \cdot CH_2CH_3 + HBr$

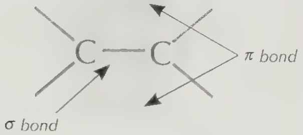
$\cdot CH_2CH_3 + Br_2 \rightarrow CH_3CH_2Br + Br\cdot$ ***(1 mark)***

Termination: $\cdot CH_2CH_3 + Br\cdot \rightarrow CH_3CH_2Br$

or $\cdot CH_2CH_3 + \cdot CH_2CH_3 \rightarrow C_4H_{10}$ ***(1 mark)***

c) Any two from: e.g. CH_3CHBr_2 / CH_3CBr_3 / CH_2BrCBr_3 / $CHBr_2CBr_3$ / CBr_3CBr_3 / CH_2BrCH_2Br / $CHBr_2CHBr_2$ ***(1 mark for each up to a maximum of 2 marks)***.

Q4 a) (i)

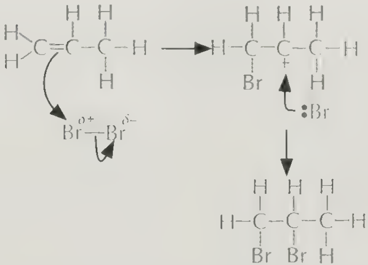


(1 mark for diagram, 1 mark for labels)

Always make sure you label any diagram you draw in the exam. You could lose marks if you don't because it's the labels that show you really know what you're talking about.

(ii) The double bond contains two pairs of electrons, so has a really high electron density / the pi bond sticks out above and below the rest of the molecule ***(1 mark)***. Electrophiles are attracted to these electron dense regions ***(1 mark)***.

b) (i)

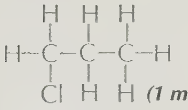


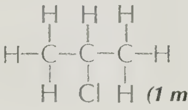
(1 mark for correct curly arrows in step 1, 1 mark for correct curly arrow in step 2, 1 one mark for correct dipole shown on Br_2, 1 mark for correct carbocation)

Make sure your curly arrows are all top-notch — they must be going from a pair of electrons/bond to the electron acceptor. Also make sure you've included the dipoles and all the charges. You'll lose marks if these are missing too.

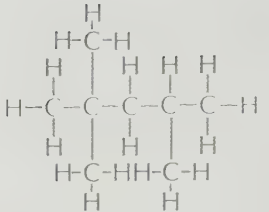
(ii) The solution would go from orange to colourless ***(1 mark)***.

c) E.g.

 ***(1 mark)***

 ***(1 mark)***

Q5 a) (i)

 ***(1 mark)***

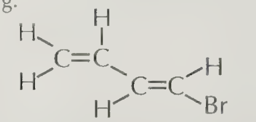
(ii) Octane would have a higher boiling point ***(1 mark)***. Octane is a straight-chain molecule. As a result there is more surface contact between octane molecules than between branched 2,2,4-trimethylpentane molecules ***(1 mark)***. This means the induced dipole-dipole interactions between the octane molecules are stronger / there are more induced dipole-dipole interactions between the molecules ***(1 mark)***. So more energy is required to overcome the induced dipole-dipole interactions and the boiling point is higher ***(1 mark)***.

b) $2C_8H_{18} + 25O_2 \rightarrow 16CO_2 + 18H_2O$ /
$C_8H_{18} + 12½O_2 \rightarrow 8CO_2 + 9H_2O$ ***(1 mark)***

c) With insufficient oxygen, incomplete combustion occurs ***(1 mark)***. Incomplete combustion of alkanes produces carbon monoxide (CO) ***(1 mark)***. Carbon monoxide binds to haemoglobin in the blood instead of oxygen, limiting the amount of oxygen that can be transported around the body and so leading to oxygen deficiency. This makes CO toxic to humans ***(1 mark)***.

Q6 a) (i) Stereoisomerism occurs when molecules have the same structural formula but a different arrangement of atoms in space ***(1 mark)***.

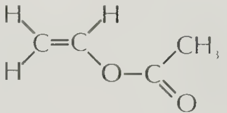
(ii) E.g.

 ***(1 mark)***

This is the E-isomer ***(1 mark)***.

b) (i) An addition polymer ***(1 mark)***.

(ii)

 ***(1 mark)***

c) Advantages: e.g. they won't permanently take up space in landfill / they avoid the need to burn plastics which produces toxic gases / they can be made from renewable materials which decreases our dependency on oil ***(1 mark for each, maximum 2 marks)***.

Disadvantages: e.g. they need specific conditions to decompose so need to be sorted from other waste / they're more expensive than oil-based equivalents ***(1 mark for each, maximum 2 marks)***.

If you're asked to discuss advantages and disadvantages, make sure you talk about both. If you only mention advantages or only talk about disadvantages you'll lose marks.

Section 2 — Alcohols and Haloalkanes

1. Properties of Alcohols

Page 246 — Application Questions

Q1 a) pentan-2-ol
b) 2-methylbutan-2-ol
c) 2,3-dimethylbutan-1-ol
d) 3-ethyl-2-methylpentane-1,5-diol

That last one is a tricky one... Make sure you have the side chains in alphabetical order and that the name has the lowest possible numbers in it.

Q2 a) secondary
b) tertiary
c) primary

Q3 Propan-1-ol, as it has a shorter non-polar carbon chain, so there's more attraction to the polar water molecules (with which the alcohols can form hydrogen bonds).
Octan-1-ol has a larger non-polar carbon chain, so there will be less attraction for the polar water molecules, and it won't mix as easily with water molecules.

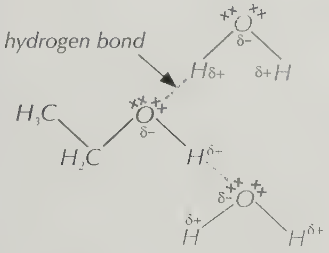
Q4 Butan-1-ol will have a higher boiling point than butane. Hydrogen bonding between the molecules in butan-1-ol means that the intermolecular forces between molecules of butan-1-ol are stronger than between the molecules in butane (which only has induced dipole-dipole interactions holding its molecules together). So it will take more energy to break the molecules apart in butan-1-ol.

Page 246 — Fact Recall Questions

Q1 -ol

Q2 A secondary alcohol is an alcohol with the -OH group attached to a carbon with two alkyl groups attached.

Q3

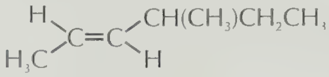


2. Reactions of Alcohols

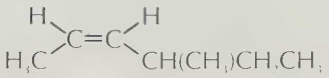
Page 248 — Application Questions

Q1 E.g. 2-methylpropan-2-ol, sodium chloride (NaCl) and a concentrated sulfuric acid catalyst at room temperature.

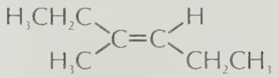
Q2 *E*-4-methyl-hex-2-ene:



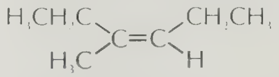
Z-4-methyl-hex-2-ene:



E-3-methyl-hex-3-ene:



Z-3-methyl-hex-3-ene:



To work out the products of the elimination reaction of an alcohol, first work out what alkenes are formed when the hydrogen atoms on either side of the hydroxyl group are eliminated. Then look to see whether either of these alkene products can form E/Z isomers.

Page 248 — Fact Recall Questions

Q1 a) $ROH + NaX \xrightarrow{H^+ \text{(catalyst)}} RX + Na^+ + H_2O$
b) nucleophilic substitution reaction

Q2 a) $CH_3CH_2OH \rightarrow CH_2CH_2 + H_2O$
b) ethene and water
c) E.g. concentrated sulfuric acid / concentrated phosphoric acid.

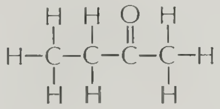
Q3 Often, two different alkene products can form depending on which side of the hydroxyl group the hydrogen atom is eliminated from. In addition, if the alkene product is able to form *E/Z* isomers, then a mixture of isomers will be formed.

3. Oxidising Alcohols

Page 252 — Application Questions

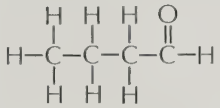
Q1 a) butanal
b) methanoic acid
c) pentan-3-one
d) hexan-2-one

Q2 a)



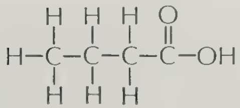
$$\begin{array}{ccccccccccc} & & H & & H & & O & & H & & \\ & & | & & | & & \| & & | & & \\ H & - & C & - & C & - & C & - & C & - & H \\ & & | & & | & & & & | & & \\ & & H & & H & & & & H & & \end{array}$$

b)



$$\begin{array}{ccccccccccc} & & H & & H & & H & & O & & \\ & & | & & | & & | & & \| & & \\ H & - & C & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & & & \\ & & H & & H & & H & & & & \end{array}$$

c)



$$\begin{array}{ccccccccccc} & & H & & H & & H & & O & & \\ & & | & & | & & | & & \| & & \\ H & - & C & - & C & - & C & - & C & - & OH \\ & & | & & | & & | & & & & \\ & & H & & H & & H & & & & \end{array}$$

You could also draw the skeletal structures of these molecules.

Page 252 — Fact Recall Questions

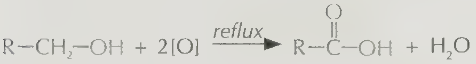
Q1 $C_2H_5OH_{(l)} + 3O_{2(g)} \rightarrow 2CO_{2(g)} + 3H_2O_{(g)}$

Q2 a) E.g. Aldehydes have the functional group C=O and have one hydrogen atom and one R group attached to the carbon atom.

b) E.g Ketones have the functional group C=O and have two R groups attached either side of the carbon atom.

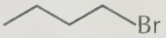
c) E.g. Carboxylic acids have the functional group COOH.

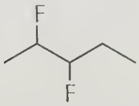
As long as you've got the basic answer right, any way that you've chosen to describe the functional groups is fine — you might have written out their formulas, or even drawn them...

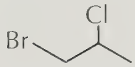
Q3

$R-CH_2-OH + 2[O] \xrightarrow{reflux} R-\overset{O}{\overset{\|}{C}}-OH + H_2O$

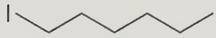
4. Haloalkanes

Page 258 — Application Questions

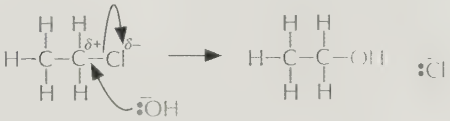
Q1 a)


b)


c)


d)


Your skeletal diagrams may look slightly different, depending on the direction you've drawn the bonds going. It doesn't matter how you've drawn it, as long as you've got the right number of each atom, and they're all joined up in the right way.

Q2


Q3 Reactions A, B and C all involve breaking a carbon-halogen bond. Reaction C would happen the quickest because the C–I bond has the lowest bond enthalpy/is the weakest of all the carbon-halogen bonds. This means that the C–I bond is the easiest to break and therefore the reaction will happen the quickest.

Q4 a) A: bromine
B: iodine
C: chlorine

b) The variables need to be kept the same so you can be sure that the only thing influencing the rate of reaction, and so the time taken for the X to disappear, is the identity of the haloalkane.

Page 258 — Fact Recall Questions

Q1 Haloalkanes contain a carbon atom which has a δ+ charge/ is electron deficient, and can attract nucleophiles.

Q2 Nucleophilic substitution reactions are reactions in which a nucleophile attacks a polar molecule and replaces a functional group.

Q3 E.g. sodium hydroxide / potassium hydroxide / water.

Q4 For a hydrolysis reaction to occur the carbon-halogen bond needs to break. The C–F bond is the strongest carbon-halogen bond/is the hardest carbon-halogen bond to break — it has the highest bond enthalpy. So fluoroalkanes are hydrolysed more slowly than other haloalkanes.

Q5 $CH_3CH_2Br + OH^- \rightarrow CH_3CH_2OH + Br^-$

Q6 E.g. You could react the haloalkane with water in the presence of silver nitrate and ethanol in a 50 °C water bath. The colour of the precipitate formed will tell you what type of haloalkane the compound is — if the precipitate is white then the compound is a chloroalkane, if the precipitate is cream then the compound is a bromoalkane, and if the precipitate is yellow then the compound is an iodoalkane.

5. Chlorofluorocarbons

Page 260 — Fact Recall Questions

Q1 A haloalkane that contains only chlorine, fluorine and carbon atoms.

Q2 E.g. $CF_2Cl_2 + h\nu \rightarrow CF_2Cl\bullet + Cl\bullet$
$Cl\bullet + O_3 \rightarrow ClO\bullet + O_2$
$ClO\bullet + O \rightarrow Cl\bullet + O_2$

The chlorine radical is regenerated and can go on to react again.

Q3 E.g. HCFCs / HFCs / hydrocarbons.

6. Global Warming

Page 263 — Fact Recall Questions

Q1 infrared radiation

Q2 E.g. carbon dioxide (CO_2), water (H_2O) and methane (CH_4).

Q3 Human activities have caused a rise in greenhouse gas concentrations. This has enhanced the greenhouse effect, which means that more heat is being trapped by the Earth's atmosphere and the Earth is getting warmer. This is global warming.

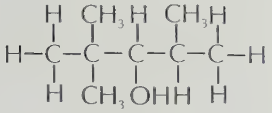
Q4 Any from: e.g. Global warming may cause oceans to expand and ice sheets in polar regions to melt. This will cause sea levels to rise, leading to more flooding. / Global warming could influence ocean currents and wind speeds. This could lead to stormier and less predictable weather. / Global warming could cause a decrease in rainfall in some areas. This will lead to droughts and crop failures, causing famines. / Global warming could cause an increase in rainfall in some areas. This could lead to flooding, which would bring diseases like cholera.

Q5 E.g. creating international treaties such as the Kyoto protocol to limit greenhouse gas emissions / using more renewable energy resources such as by using wind turbines and solar panels / using less non-renewable energy resources such as coal power stations / encouraging the use of more energy-efficient electrical appliances such as energy-saving light bulbs and electric cars.

Exam-style Questions — pages 265-266

1 A ***(1 mark)***

If you draw the molecule out, you'll see there's only one hydrogen atom on the carbon atoms adjacent to the -OH carbon:



This means only one alkene can form, and since this alkene can't form E/Z isomers, there's only one product.

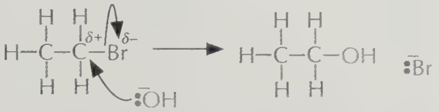
2 B ***(1 mark)***

3 C ***(1 mark)***

4 a) (i) $CH_3CH_2Br + OH^- \rightarrow CH_3CH_2OH + Br^-$ ***(1 mark)***

You'd also get the mark if you included the Na^+ ions in the equation, like this: $CH_3CH_2Br + NaOH \rightarrow CH_3CH_2OH + NaBr$

(ii)



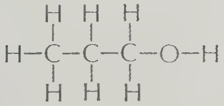
(3 marks, 1 mark for each correct curly arrow and 1 mark for the C–Br dipole correctly shown.)

(iii) The reaction of sodium hydroxide with iodoethane would be quicker than the reaction of bromoethane with sodium hydroxide ***(1 mark)***. This is because the C–I bond is weaker than the C–Br bond / the bond enthalpy of the C–I bond is lower than that of the C–Br bond, which means it is more easily broken ***(1 mark)***.

b) (i) The hydroxyl groups can form hydrogen bonds with the water molecules ***(1 mark)***.

(ii) In butan-1-ol, more of the molecule is a non-polar carbon chain, which doesn't mix easily with water molecules ***(1 mark)***.

5 a) Molecule **A** is propan-1-ol ***(1 mark)***:



(1 mark)

If you're asked to draw a displayed formula, remember that you've got to draw all the bonds — even the one between oxygen and hydrogen in the -OH group.

b) Acidified potassium dichromate(VI)/$K_2Cr_2O_7$ and H_2SO_4 ***(1 mark)***. Heat under reflux ***(1 mark)***.

6 a) Ozone in the atmosphere forms a layer which absorbs UV radiation and acts as a chemical sunscreen ***(1 mark)***.

b) CFCs undergo homolytic fission with UV light to form chlorine radicals ***(1 mark)***. These chlorine radicals act as catalysts in the breakdown of ozone ***(1 mark)***.

c) E.g. $NO\bullet + O_3 \rightarrow NO_2 + O_2$ ***(1 mark)***
$NO_2 + O \rightarrow NO\bullet + O_2$ ***(1 mark)***
Overall: $O_3 + O \rightarrow 2O_2$ ***(1 mark)***

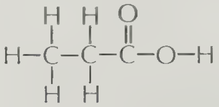
Section 3 — Analysis and Organic Synthesis

1. Infrared Spectroscopy

Pages 270-271 — Application Questions

Q1 a) A (~3000 cm^{-1}, broad) — O–H (carboxylic acid)
B (~1700 cm^{-1}) — C=O

b)



The mass of the carboxylic acid group (COOH) is 45 (12 + 16 + 16 + 1). The M_r of the molecule is 74, so the rest of the molecule has a mass of 74 – 45 = 29. This corresponds to an ethyl group (CH_3CH_2), so the molecule must be propanoic acid.

Q2 E.g. There is a strong, sharp peak at about 1700 cm^{-1}. This indicates that a C=O bond is present in the molecule.

Q3 Spectrum A.

O–H bonds in an alcohol create a strong absorption at around 3200-3600 cm^{-1}. Spectrum A has this absorption and Spectrum B doesn't — so Spectrum A must be propan-2-ol.

Q4

Bond	Frequency / Wavenumber (cm^{-1})
C–C	750 – 1100
C=C	1620 – 1680
C=O	1630 – 1820
C–H	2850 – 3100

Page 271 — Fact Recall Questions

Q1 A beam of IR radiation is passed through a sample of a chemical. Some of the IR radiation is absorbed by the covalent bonds in the molecules, increasing their vibrational energy. Bonds between different atoms absorb different frequencies of IR radiation. Bonds in different places in a molecule absorb different frequencies too. The percentage of IR radiation transmitted at each frequency is plotted to give an IR spectrum.

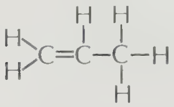
Q2 E.g. If a person's suspected of drink-driving, they can be breathalysed by the roadside. If it says that the driver's over the limit, they're taken into a police station for a more accurate test using infrared spectroscopy. The amount of ethanol vapour in the driver's breath is found by measuring the intensity of the peak corresponding to the C–H bond in the IR spectrum. / Infrared spectroscopy can be used to monitor the levels of pollutant gases such as CO or NO. The intensity of the peaks corresponding to the C≡O or N=O bonds are used to monitor their levels.

2. Mass Spectrometry

Page 275 — Application Questions

Q1 E.g. CH_3^+ / $CH_3CH_2^+$ / CH_2^+ / $CH_3CH_2CH_2^+$ / OH^+.

Q2 The molecule is propene.



This table shows some of the m/z peaks from the mass spectrum and the fragment ions they can be assigned to:

m/z	fragment ion
15	CH_3^+
27	CH_2CH^+
41	$CH_3CCH_2^+$
42	$CH_3CHCH_2^+$ (molecular ion)

Don't forget that you don't have to assign all of these peaks — just as long as you've done enough to be able to prove that it's propene...

Q3 E.g. $CH_3CH_2CHOH^+$ / CH_3CHOH^+.

Page 275 — Fact Recall Questions

Q1 The *x*-axis tells you the mass/charge ratio and the *y*-axis tells you the relative abundance of the molecular ion.

Q2 The molecular mass of the compound.

Q3 CH_3^+

3. Combined Techniques

Page 278 — Application Questions

Q1 B

The M peak on the mass spectrum appears at an m/z of 72, so the M_r of the compound will be 72. Both A and B have $M_r = 72$, but C has $M_r = 58$, so the compound is not C.

Looking at the IR spectrum, there is an intense peak at about 1700 cm^{-1}. This is the peak for a C=O bond, which shows that the molecule is B, since it has a ketone group (A has no carbonyl group).

Q2 First, work out the empirical formula from the percentage composition:

In 100 g of compound there will be 54.5 g of carbon, 9.01 g of hydrogen and 36.4 g of oxygen.

Use the formula moles = mass ÷ M_r to find the number of moles:

C: $\frac{54.5}{12} = 4.54$ mol H: $\frac{9.01}{1} = 9.01$ mol

O: $\frac{36.4}{16} = 2.28$ mol

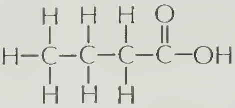
Divide each number of moles by the smallest number (2.28)

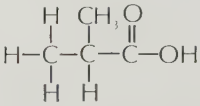
C: 2 H: 4 O: 1

The ratio of C : H : O is 2 : 4 : 1, so the empirical formula is C_2H_4O, which has an M_r of $[(2 \times 12) + (4 \times 1) + 16] = 44$.

Looking at the mass spectrum, the compound has a parent ion peak at $m/z = 88$, which is twice the mass of the empirical formula. So the molecular formula is $C_4H_8O_2$.

The spectrum has a peak at an m/z of 45, which could be a $COOH^+$ fragment, so the compound is likely to be a carboxylic acid. The carboxylic acids with molecular formula of $C_4H_8O_2$ are butanoic acid and 2-methylpropanoic acid:





As well has the $COOH^+$ fragment, butanoic acid will have the fragment CH_2COOH^+ (59 m/z), and there is no fragment of equivalent mass formed by 2-methylpropanoic acid. Meanwhile 2-methylpropanoic acid will form the fragment $CHCOOH^+$ (58 m/z), and there is no fragment of equivalent mass formed by butanoic acid. The mass spectrum has a peak at 59 m/z, but no peak at 58 m/z.

This shows that the compound is **butanoic acid**.

4. Practical Techniques in Organic Synthesis

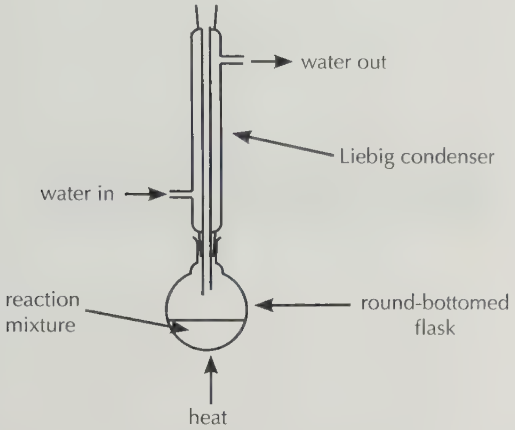
Page 281 — Application Questions

Q1 E.g. Redistil the mixture, as hexane will distil out of the mixture at a lower temperature than ethanol, so the two liquids can be collected separately. / Use a separating funnel to separate hexane (insoluble in water) from ethanol (soluble in water). You'll be left with an organic layer containing hexane and an aqueous layer containing water and ethanol. The ethanol can be separated from the water by redistillation (as ethanol has a lower boiling point than water) or can be dried using an anhydrous salt, e.g. $MgSO_4$ or $CaCl_2$, which can then be removed by filtration.

Q2 Jomei could carry out the reaction in a distillation apparatus, as the product would distil out of the reaction mixture as it formed, and so it wouldn't be over-oxidised.

Page 281 — Fact Recall Questions

Q1



Q2 The different boiling points of the compounds.

Q3 E.g. anhydrous magnesium sulfate ($MgSO_4$) and anhydrous calcium chloride ($CaCl_2$).

5. Organic Synthesis

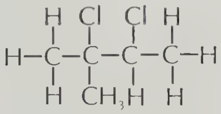
Page 284 — Application Questions

Q1 Carboxylic acid, alkene and a haloalkane.

Q2 a) Sodium chloride (NaCl) and a concentrated acid catalyst (e.g. H_2SO_4) at room temperature.

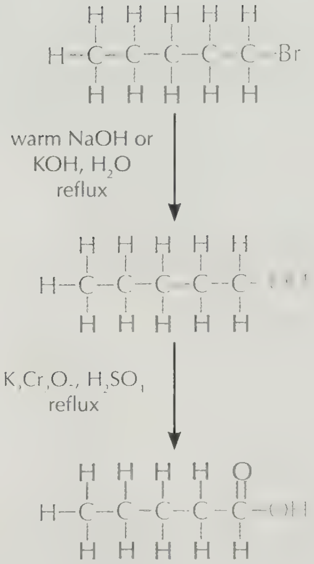
b) Concentrated acid (e.g. H_2SO_4 or H_3PO_4) and heat.

c)



$CH_3C(Cl)(CH_3)CHClCH_3$

Q3 E.g.



Page 284 — Fact Recall Questions

Q1 a) an alkene

b) an aldehyde

c) a carboxylic acid

Q2 a) nucleophilic substitution

b) radical substitution

c) e.g. nucleophilic substitution / dehydration / elimination / oxidation

Q3 H_2, nickel catalyst, 150 °C.

Q4 It would be oxidised from to an aldehyde and then to a carboxylic acid.

Exam-style Questions — pages 286-288

Q1 D ***(1 mark)***

Q2 B ***(1 mark)***

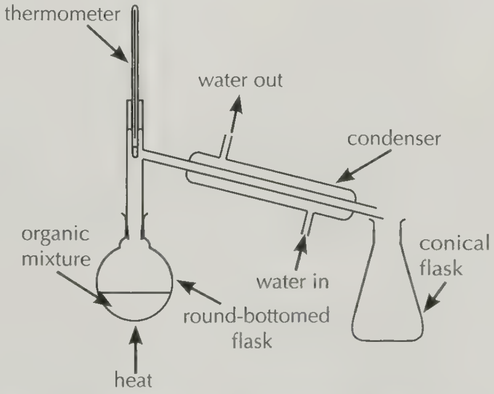
Q3 B ***(1 mark)***

Q4 a) hex-3-ene ***(1 mark)***

b) e.g. steam ***(1 mark)***, H_3PO_4 catalyst, 300 °C, 60-70 atm ***(1 mark)***

c) E.g. the IR spectrum of hexan-3-ol would have a peak at about 3200-3600 cm^{-1} that is not in the spectrum of hex-3-ene, due to the presence of the -OH group / The IR spectrum of hex-3-ene would have a peak at about 1620-1680 cm^{-1} that is not in the spectrum of hexan-3-ol, due to the presence of the C=C bond ***(1 mark)***.

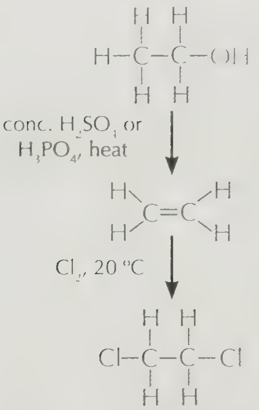
d) E.g.



(3 marks — 1 mark for correct apparatus, 1 mark for a working system, e.g. open system, thermometer bulb level with outlet, correct direction of water flow, 1 mark for correct labels.)

e) E.g. the mass spectrum shows that hexan-3-ol has been synthesised ***(1 mark)***. The M peak is at $m/z = 102$, which is the same as the relative formula mass of hexan-2-ol ***(1 mark)***. There is also a peak at $m/z = 73$ which matches the mass of a $CH_3CH_2CH_2CHOH^+$ fragment, and a peak at $m/z = 59$ which matches the mass of a $CH_3CH_2CHOH^+$ fragment ***(1 mark)***.

Q5 a)



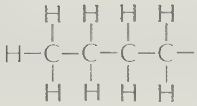
(4 marks — 1 mark for correct synthetic route going via an alkene, 1 mark for correct reagents and conditions in step 1, 1 mark for correct reagents in step 2, 1 mark for correct intermediate.)

b) E.g. redistillation ***(1 mark)***.

Q6 a) If a person's suspected of drink-driving, they may be breathalysed using infrared spectroscopy ***(1 mark)***. The amount of ethanol vapour in the driver's breath is found by measuring the intensity of the peak corresponding to the C–H bond in the IR spectrum ***(1 mark)***.

b) You can tell similar molecules apart using mass spectrometry because they won't produce exactly the same set of fragments ***(1 mark)***.

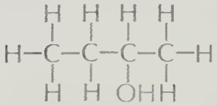
c) The molecular ion peak has an m/z of 58 and so the M_r of the compound is 58 ***(1 mark)***.
The peak at $m/z = 15$ could be caused by a CH_3^+ fragment ion. The peak at $m/z = 29$ could be caused by a $CH_3CH_2^+$ fragment ion. The peak at $m/z = 43$ could be caused by a $CH_3CH_2CH_2^+$ fragment ion. ***(1 mark for each correctly assigned fragment up to a maximum of 2 marks)***
The molecule is butane.



(1 mark)

There are only two hydrocarbons with an M_r of 58 — butane and 2-methylpropane. Molecule J has a strong mass spectrum peak at $m/z = 29$, so it can't be 2-methylpropane because that doesn't have a peak there.

d) The infrared spectrum shows a strong broad peak at about 3300 cm^{-1}, which corresponds to an O–H group on an alcohol ***(1 mark)***. Acidified potassium dichromate(VI) will oxidise secondary alcohols under reflux to ketones — so molecule **K** must be a secondary alcohol ***(1 mark)***. The only secondary alcohol with an M_r of 74 is butan-2-ol ***(1 mark)***.
So molecule **K** is butan-2-ol.



(1 mark)

Module 5

Section 1 — Reaction Rates

1. Monitoring Reactions

Page 292 — Application Questions

Q1 a) E.g. measure the change in pH using a pH meter.

b) E.g. measure the loss of mass using a mass balance / measure the volume of gas produced using a gas syringe / measure the change in pH using a pH meter.

c) E.g. use colorimetry to measure the change in absorbance / measure the loss of mass using a mass balance / measure the volume of gas produced using a gas syringe.

Q2 The calculated rate would be less than the true rate. Not all of the gas produced would be collected, as some would escape from the system. This means that the reaction would appear to have produced less gas than it really had, and so the rate would appear lower.

Q3 Initial number of moles HCl = conc × vol
= 1.50 × (250 ÷ 1000)
= 0.375

Time / seconds	Mass lost / g	Concentration of HCl / mol dm^{-3}
0	0.00	**1.50**
10	0.600	**1.36**
20	1.18	**1.22**
30	1.77	**1.08**
40	2.37	**0.942**
50	2.94	**0.808**
60	3.51	**0.674**

Q4 $Na_2CO_3 + H_2SO_4 \rightarrow Na_2SO_4 + H_2O + CO_2$
Initial number of moles H_2SO_4 = conc × vol
= 1.00 × (100 ÷ 1000)
= 0.100

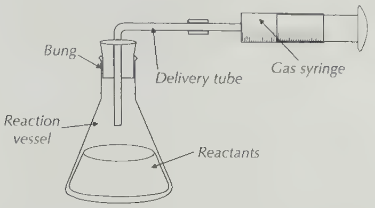
Time / seconds	Concentration of H_2SO_4 / mol dm^{-3}
0	**1.00**
15	**0.999**
30	**0.997**
45	**0.996**
60	**0.995**
75	**0.984**

See page 291 for a full method for this type of question.

Page 292 — Fact Recall Questions

Q1 Continuous monitoring is a method for following the progress of a reaction. It involves taking measurements at regular intervals, over the course of a reaction, to measure the loss of a reactant or the formation of a product.

Q2 e.g.



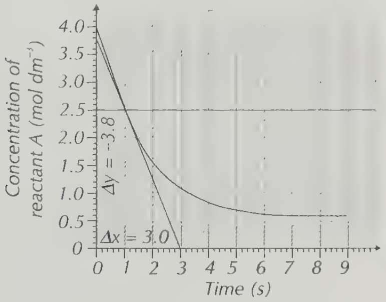
Q3 Colorimeters measure the absorbance of a particular wavelength of light by a solution.

Q4 E.g. you could measure the loss of mass, at regular intervals, as a gaseous product forms and escapes. By carrying out the reaction on a balance, you can follow how the mass changes throughout the experiment. / You could collect the gas in a gas syringe and record the volume of gas produced, at regular intervals, over the course of the reaction.

2. Concentration-Time Graphs

Page 294 — Application Questions

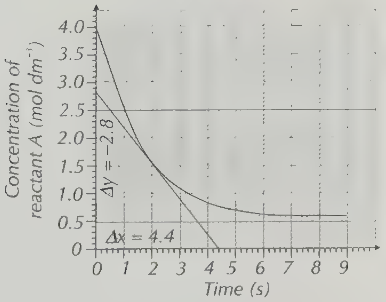
Q1 a)



$$\text{Rate} = \frac{\Delta y}{\Delta x} = \frac{-3.8}{3.0} = \mathbf{-1.3\ mol\ dm^{-3}\ s^{-1}}$$

Drawing tangents accurately is tricky so there may be some variation between the answer you got and the 'official' answer. Don't worry though — in the exam, you'll usually be allowed a range of answers if you're asked to calculate a gradient. So for part a) allow yourself anything from −0.9 to −1.7.

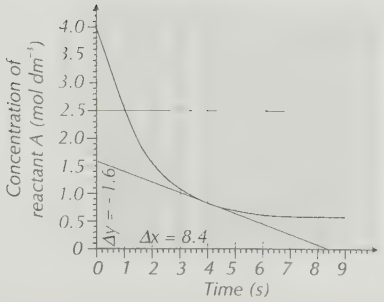
b)



$$\text{Rate} = \frac{\Delta y}{\Delta x} = \frac{-2.8}{4.4} = \mathbf{-0.64\ mol\ dm^{-3}\ s^{-1}}$$

For part b) anything from −0.44 to −0.84 is OK.

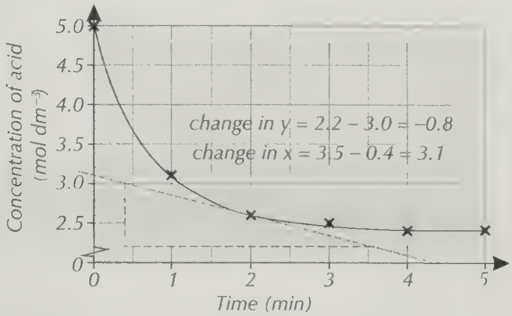
c)



$$\text{Rate} = \frac{\Delta y}{\Delta x} = \frac{-1.6}{8.4} = \mathbf{-0.19\ mol\ dm^{-3}\ s^{-1}}$$

For part c) anything from −0.13 to −0.25 will do.

Q2 a)



b) see above

c) E.g. gradient = change in y ÷ change in x

$= -0.8 \div 3.1 = -0.258...$

So the rate is **0.26 mol dm^{-3} min^{-1} (2 s.f.)**

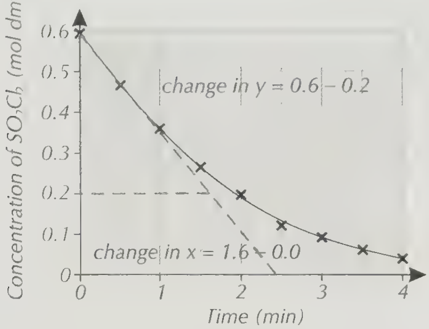
Page 294 — Fact Recall Question

Q1 Measure the gradient of the graph / the gradient of a tangent to the graph at that particular time. The gradient is equal to the rate of reaction.

3. Initial Rates

Page 298 — Application Questions

Q1 E.g.



Gradient = change in y ÷ change in x
= (0.20 – 0.60) ÷ (1.6 – 0.0)
= –0.4 ÷ 1.6 = –0.25

So the rate is **0.25 mol dm^{-3} min^{-1} (2 s.f.)**

Q2 The rate of each reaction = $\frac{20\ cm^3}{\text{time taken}}$

Trial number	[illegible] / mol dm^{-3}	Time to produce 20 cm^3 $H_{2(g)}$ / s	Initial rate / cm^3 s^{-1}
1	1.25	5.1	3.9
2	0.800	15.3	1.3
3	0.500	31.5	0.63

Page 298 — Fact Recall Questions

Q1 Measure the gradient of a concentration-time graph at time = 0 s

Q2 E.g. The concentration of each reactant doesn't change significantly over the time period of your clock reaction / the temperature stays constant / when the endpoint is seen, the reaction has not proceeded too far.

4. Reaction Orders

Page 302 — Application Questions

Q1 a) Looking at experiments 1 and 2: doubling [O_3] doubles the rate so the reaction is order 1 with respect to O_3. Looking at experiments 2 and 3: tripling [C_2H_4] triples the rate so the reaction is order 1 with respect to C_2H_4.

b) Overall order = order with respect to [O_3] + order with respect to [C_2H_4] = 0 + 1 = **1**

The overall order is the sum of the orders with respect to each reactant.

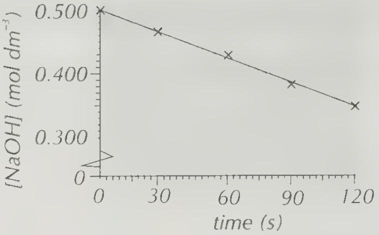
Q2 a) A = first order
B = zero order
C = second order

b) (i) If [A] was halved the rate of reaction would also halve.

(ii) If [B] was tripled the rate of reaction would stay the same.

(iii) If [C] was doubled, the reaction rate would increase by a factor of four (quadruple).

Q3



The concentration-time graph is a straight line, so the reaction is zero order with respect to NaOH.

Q4 Looking at experiments 1 and 2: doubling [B] quadruples the rate so the reaction is order 2 with respect to B. Looking at experiments 2 and 3: tripling [C] triples the rate so the reaction is order 1 with respect to C. Look at experiments 2 and 4: the reaction is first order with respect to C so, doubling [C] will double the rate of reaction to 2.00 mol dm^{-3} s^{-1}. So halving [A] must have halved the reaction rate back down to 1.00 mol dm^{-3} s^{-1}. This means that the reaction is first order with respect to A.

You could also work out the order with respect to A from experiments 3 and 4. Decreasing [C] by a third decreases the rate from 3.00 mol dm^{-3} s^{-1} to 2.00 mol dm^{-3} s^{-1}. Halving [A] decreases the rate from 2.00 mol dm^{-3} s^{-1} to 1.00 mol dm^{-3} s^{-1}, so the reaction must be first order with respect to A.

Page 302 — Fact Recall Questions

Q1 The reaction order with respect to a particular reactant tells you how the reactant's concentration affects the rate of reaction.

Q2 a) E.g. find the gradient at various points along a concentration-time graph. Plot rate of reaction against concentration to produce a rate-concentration graph / Find the initial rate of the reaction at varying initial concentrations of one of the reactants, and plot the initial rate of the reaction against the initial reactant concentration to produce a rate-concentration graph.

b) The shape of the rate-concentration graph indicates the order of reaction (horizontal line = zero order, straight line through the origin = first order, curve = second order).

5. Rate Equations

Page 304 — Application Question

Q1 a) Rate = $k[Na_2S_2O_3]$

b) Rate = 4.67 × 10^{-1} × 0.45 = **0.21 mol dm^{-3} s^{-1}**

Even though you're given the concentration of HCl in the question, you don't need to use it in your calculation, as [HCl] isn't in the rate equation.

Page 304 — Fact Recall Questions

Q1 The rate equation tells you how the rate of a reaction is affected by the concentration of the reactants.

Q2 a) The rate constant.
b) The concentration of reactant A.
c) The order of the reaction with respect to A.

Q3 rate = $k[A]^m[B]^n[C]^x$

6. The Rate Constant

Page 308 — Application Questions

Q1 a) Rate = $k[NO]^2[Cl_2]$

b) $5.85 \times 10^{-6} = k(0.400)^2(0.400)$ so

$$k = \frac{5.85 \times 10^{-6}}{[0.400]^2[0.400]} = 9.14 \times 10^{-5}$$

Now find the units for k:

$$k = \frac{\text{mol dm}^{-3}\,\text{s}^{-1}}{(\text{mol dm}^{-3})^2(\text{mol dm}^{-3})} = \text{mol}^{-2}\,\text{dm}^6\,\text{s}^{-1}$$

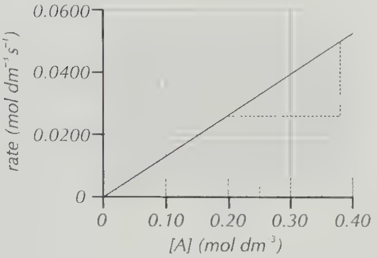
k = **9.14×10^{-5} mol^{-2} dm^6 s^{-1}**

c) Rate = $k[NO]^2[Cl_2]$

Rate = $(9.14 \times 10^{-5}) \times (0.500)^2 \times 0.200$

= **4.57×10^{-6} mol dm^{-3} s^{-1}**

Q2 *For a first order reaction, the rate constant is equal to the gradient of its rate-concentration graph:*



E.g. gradient = change in $y \div$ change in x

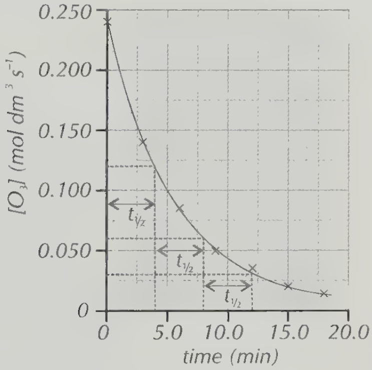
= $(0.0500 - 0.0260) \div (0.38 - 0.20)$

= $0.024 \div 0.18 = 0.13$

Now find the units for k: $k = \frac{\text{mol dm}^{-3}\,\text{s}^{-1}}{(\text{mol dm}^{-3})} = \text{s}^{-1}$

k = **0.13 s^{-1}**

Q3 a)



$[O_3]$ from 0.240 to 0.120 mol dm^{-3} = **4.0 minutes**

$[O_3]$ from 0.120 to 0.060 mol dm^{-3} = **4.0 minutes**

$[O_3]$ from 0.060 to 0.030 mol dm^{-3} = **4.0 minutes**

b) The half-life is always 4.0 minutes, so the reaction is first order with respect to $[O_3]$.

$$k = \frac{\ln 2}{t_{1/2}}$$

You first have to convert the half-life from minutes into seconds:

$t_{1/2} = 4.0 \times 60 = 240$ s

$k = \frac{\ln 2}{240}$ = **2.9×10^{-3} s^{-1}**

Page 308 — Fact Recall Questions

Q1 Measure the gradient of the line of best fit (a straight line), which is equal to the rate constant of the reaction.

Q2 The half-life of a reaction is the amount of time it takes for half of the reactant to be used up.

Q3 $k = \frac{\ln 2}{t_{1/2}}$

7. The Rate-Determining Step

Page 312 — Application Questions

Q1 Rate = $k[A]^2[B]$

Don't forget to include the rate constant in your answer. If you've just written rate = [A]²[B], your answer's not right, even though you've done all the hard work working out the reaction orders.

Q2 Rate = $k[Br_2][NO]$

Q3 a) Step 1. The rate equation shows that the rate-determining step involves two molecules of NO_2, and there are two NO_2 molecules in step 1.

Don't forget — if it's in the rate equation it must be involved in the rate-determining step.

b) If the reaction had a one-step mechanism, that step would have to involve CO. CO is not in the rate equation so can't be involved in the rate-determining step. So a one-step mechanism isn't possible.

Q4 E.g. $O_{3\,(g)} \rightarrow O_{2\,(g)} + O\bullet_{(g)}$

$O\bullet_{(g)} + O_{3\,(g)} \rightarrow 2O_{2\,(g)}$

If you didn't get this answer don't worry. As long at the equations add up to the overall equation, the first step (the rate-determining step) only involves one molecule of O₃ and your equations are balanced you can have the mark.

Q5 E.g. $H_2O_{2\,(aq)} + I^-_{(aq)} \rightarrow H_2O_{(l)} + IO^-_{(aq)}$

$H_2O_{2\,(aq)} + IO^-_{(aq)} \rightarrow H_2O_{(l)} + O_{2\,(g)} + I^-_{(aq)}$

Don't forget — if you're given a reaction involving a catalyst, make sure the catalyst is regenerated at the end. If the catalyst hasn't been regenerated then you must have gone wrong somewhere.

Page 312 — Fact Recall Questions

Q1 The rate-determining step is the slowest step in a reaction mechanism, so it's the step which determines the overall rate of the reaction.

Q2 2

Q3 1

8. The Arrhenius Equation

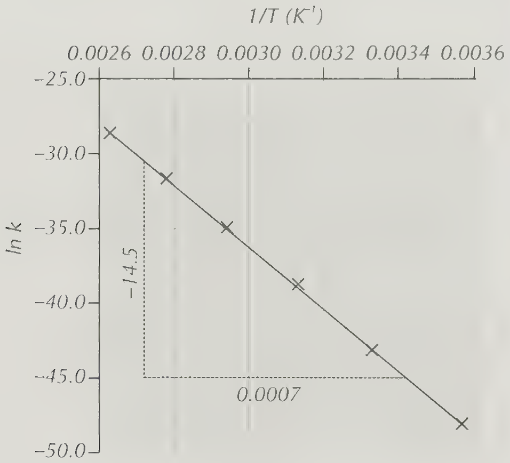
Page 316 — Application Questions

Q1 a) Reaction B will have a larger rate constant, as the activation energy is lower than Reaction A. This means that the $\frac{-E_a}{RT}$ term will be smaller and less negative, so the rate constant, k, will be greater since $k = Ae^{\frac{-E_a}{RT}}$.

b) The reaction at 45 °C will be faster than the reaction at 30 °C. This is because a larger value of T causes the $\frac{-E_a}{RT}$ term in the Arrhenius equation to be smaller and less negative, so $k = Ae^{\frac{-E_a}{RT}}$ will be greater. A larger value of k means a faster rate of reaction.

Q2 a) *To draw the Arrhenius plot, you first have to calculate ln k and $1/T$.*

Temperature (K)	k ($dm^3\ mol^{-1}\ s^{-1}$)	$1/T$ (K^{-1})	ln k
280	1.25×10^{-21}	0.00357	–48.131
300	1.79×10^{-19}	0.00333	–43.167
320	1.38×10^{-17}	0.00313	–38.822
340	6.34×10^{16}	0.00294	–34.994
360	1.91×10^{-14}	0.00278	–31.589
380	4.02×10^{13}	0.00263	28.542



b) Gradient = $\frac{-E_a}{R} = \frac{\text{change in } y}{\text{change in } x} = \frac{-14.5}{0.0007} = -20\ 714...$

$-E_a = -20\ 714... \times 8.31 = -\ 172\ 135...\ J\ mol\ ^1$

E_a = **172 kJ mol⁻¹**

If you've drawn this graph with a sensible scale, it probably won't show the y-intercept, so the best way to find A is by substituting your value for E_a back into the Arrhenius equation.

c) $\ln k = \frac{-E_a}{RT} + \ln A$

When $\ln k = -34.994$, $1/T = 0.00294$

So $-34.994 = -\ (0.00294 \times \frac{172\,135...}{8.31}) + \ln A$

$\ln A = -34.994 + 60.9$

$\ln A = 25.9...$

$A = e^{25.9...}$ = **1.78×10^{11} mol dm⁻³ s⁻¹**

If you calculated A using the y intercept, you should have found that ln A = 26.3, so A = $e^{26.3} = 2.6 \times 10^{11}$ mol dm⁻³ s⁻¹.

Page 316 — Fact Recall Questions

Q1 a) The rate constant, units vary.

b) The activation energy, in J mol⁻¹.

c) The temperature, in K.

d) The pre-exponential factor, units vary but are the same as the rate constant.

Q2 $\ln k = \frac{-E_a}{RT} + \ln A$

Q3 The gradient is equal to the value of $\frac{-E_a}{R}$, so can be used to find the activation energy of the reaction.

Exam-style Questions — Pages 318-320

1 C ***(1 mark)***

2 A ***(1 mark)***

rate = $k[A][B]^2$, so k = rate ÷ ($[A][B]^2$)

= 0.00238 ÷ (0.426 × 0.775²) = 0.00930 mol⁻² dm⁶ s⁻¹

3 D ***(1 mark)***

4 B ***(1 mark)***

5 a) The reaction is first order with respect to H_2 ***(1 mark)*** and second order with respect to NO ***(1 mark)***.

Finding the reaction order with respect to NO is tricky. You know the reaction is first order with respect to H_2 from experiments 1 and 2, so if only $[H_2]$ changed from experiment 2 to 3 you would expect the rate of reaction to halve. But the rate of reaction is four times greater than this, so the reaction must be second order with respect to NO.

b) rate = $k[H_2][NO]^2$ ***(1 mark)***

c) rate = $k[H_2][NO]^2$ so k = rate ÷ $[H_2][NO]^2$

E.g. Using experiment 1:

$k = (4.5 \times 10^{-3}) \div (6 \times 10^{-3})(3 \times 10^{-3})^2 = 8.3 \times 10^4$

$k = mol\ dm^{-3}\ s^{-1} \div (mol\ dm^{-3})(mol\ dm\ ^{-3})^2 = mol^{-2}\ dm^6\ s^{-1}$

k = **8.3 × 10⁴ mol⁻² dm⁶ s⁻¹**

(3 marks for correct answer, otherwise 1 mark for correct method and 1 mark for correct units.)

d) rate = $k[H_2][NO]^2$

$= (8.3 \times 10^4) \times (2.5 \times 10^{-3}) \times (4.5 \times 10^{-3})^2$

= **4.2 × 10⁻³ mol dm⁻³ s⁻¹**

(1 mark for correct value, 1 mark for correct units — full marks if the method is correct but error carried forward from (c).)

If you used 6.5×10^5 as your value for k, an answer of rate = 0.0329 mol dm⁻³ s ¹ will get you full marks.

e) (i) The rate equation shows that the rate-determining step involves 2 molecules of NO and 1 molecule of H_2 ***(1 mark)***. There are 2 molecules of H_2 in the overall equation so there must be another step involving another molecule of H_2 ***(1 mark)***.

(ii) A possible mechanism for this reaction would be:

Step 1: $2NO + H_2 \rightarrow N_2O + H_2O$

Step 2: $N_2O + H_2 \rightarrow H_2O + N_2$

(1 mark for the left hand side of step 1, 1 mark for rest of step 1 and step 2.)

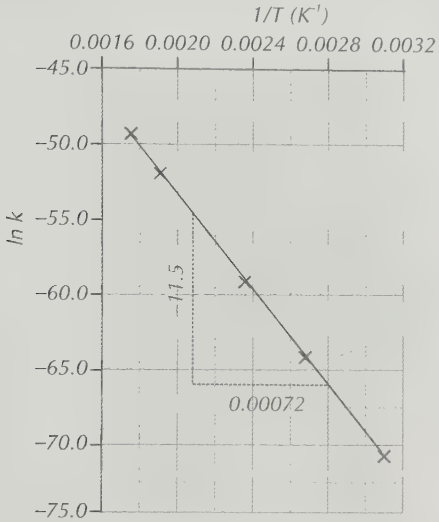
Other mechanisms are possible and will gain credit as long as:

- *The reactants in the first equation are 2NO and H_2.*
- *The steps add together to give the overall reaction.*
- *Both equations are balanced.*

6 a)

T / °C	k / $mol^{-1}\ dm^3\ s^{-1}$	T / K	$1/T$ / K^{-1}	ln k
50	1.96×10^{-31}	323	0.00310	–70.7
100	1.36×10^{-28}	373	0.00268	–64.2
150	2.01×10^{-26}	423	0.00236	–59.2
250	2.50×10^{-23}	523	0.00191	–52.0
300	3.47×10 [illegible]	573	0.00175	–49.4

(2 marks — 1 mark for correctly converting T (°C) values into 1/T (K^{-1}), 1 mark for correctly converting k ($mol^{-1}\ dm^3\ s^{-1}$) values into ln k.)



(3 marks — 1 mark for correct axes with reasonable scale, 1 mark for correctly plotted points, 1 mark for line of best fit.)

b) (i) Gradient = $\frac{-E_a}{R} = \frac{-11.5}{0.00072} = -15\ 972$ ***(1 mark)***

$E_a = 15\ 972 \times 8.31 = 132\ 729...\ J\ mol^{-1}$

= 133 kJ mol⁻¹ ***(1 mark — allow between 120 and 146 kJ mol⁻¹)***

(ii) $\ln k = \frac{-E_a}{RT} + \ln A$

When $\ln k = -66.0$, $1/T = 0.0028\ K^{-1}$

$-66.0 = -(0.0028 \times \frac{132\ 729...}{8.31}) + \ln A$

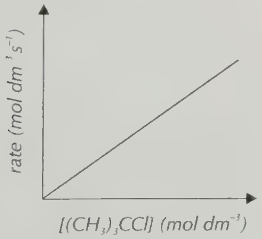
$\ln A = -66.0 + 44.7... = -21.2...$ ***(1 mark)***

$A = e^{-21.2...} =$ **$5.7 \times 10^{-10}\ mol^{-1}\ dm^3\ s^{-1}$** ***(1 mark – allow between 7.62×10^{-12} and 5.06×10^{-8})***

If you plotted a graph that showed the y-intercept through the y-axis at $x = 0$, then you could have calculated A by finding the y-intercept. The y-intercept you found should have been –21.9, so $A = e^{-21.9} = 3.1 \times 10^{-10}$.

7 a) (i) First order ***(1 mark)***.

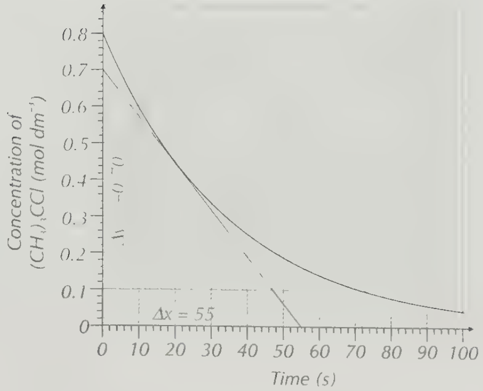
(ii)



(1 mark)

b) rate = $k[(CH_3)_3CCl]$ ***(1 mark)***

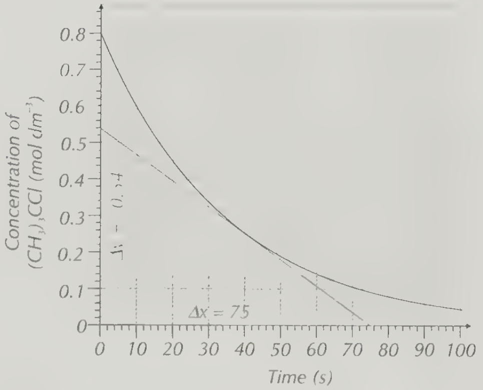
c) (i)



Rate = $\frac{\Delta y}{\Delta x} = \frac{-0.70}{55} = 0.013\ mol\ dm^{-3}\ s^{-1}$

(1 mark — allow between 0.008 and 0.017)

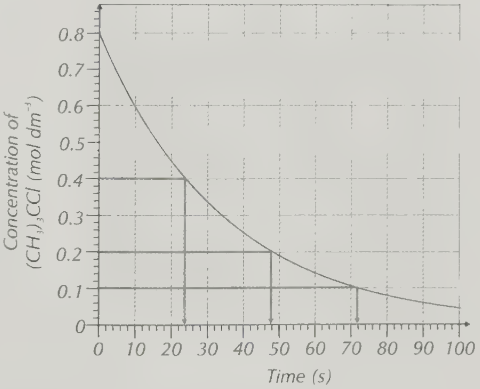
(ii)



Rate = $\frac{\Delta y}{\Delta x} = \frac{-0.54}{75} = 0.0072\ mol\ dm^{-3}\ s^{-1}$

(1 mark — allow between 0.0048 and 0.0096)

d)



The half-life is **24 seconds** ***(1 mark)***.

e) The reaction is first order, so $k = \frac{\ln 2}{t_{½}} = \frac{\ln 2}{24} =$ **$0.029\ s^{-1}$** ***(1 mark)***

f) rate = $k[(CH_3)_3CCl] = 0.029 \times 1.35$

= **$0.0392\ mol\ dm^{-3}\ s^{-1}$** ***(1 mark)***

g) E.g. First step: $(CH_3)_3CCl \rightarrow (CH_3)_3C^+ + Cl^-$ ***(1 mark)***

Second step: $(CH_3)_3C^+ + OH^- \rightarrow (CH_3)_3COH$ ***(1 mark)***

Other mechanisms are possible and will gain credit as long as:

- The only reactant in the first equation is $(CH_3)_3CCl$.
- The steps add together to give the overall reaction.
- Both equations are balanced.

Section 2 — Equilibrium

1. The Equilibrium Constant

Pages 325-326 — Application Questions

Q1 a) $K_c = \frac{[C_2H_5OH]}{[C_2H_4][H_2O]}$

b) The equation tells you that if 1 mole of C_2H_5OH decomposes, 1 mole of C_2H_4 and 1 mole of H_2O are formed. So if 1.85 moles of C_2H_4 are produced at equilibrium, there will also be **1.85** moles of H_2O. 1.85 moles of C_2H_5OH has decomposed so there must be 5 – 1.85 = **3.15** moles of C_2H_5OH remaining.

c) The volume of the reaction is 15.0 dm^3. So the molar concentrations are:
$[H_2O] = [C_2H_4] = 1.85 \div 15.0 =$ **0.123 mol dm^{-3}**.
$[C_2H_5OH] = 3.15 \div 15.0 =$ **0.210 mol dm^{-3}**.

d) $K_c = \frac{[C_2H_5OH]}{[C_2H_4][H_2O]} = \frac{0.210}{(0.123)(0.123)} = 13.9$

units of $K_c = \frac{(\text{mol dm}^{-3})}{(\text{mol dm}^{-3})(\text{mol dm}^{-3})} = \frac{1}{(\text{mol dm}^{-3})}$

K_c = **13.9 mol^{-1} dm^3**

Setting your answer out like this makes it clear to the examiner what you've done and means you're more likely to pick up some method marks.

e) $K_c = \frac{[C_2H_5OH]}{[C_2H_4][H_2O]}$ so $3.8 = \frac{0.80}{[C_2H_4][H_2O]}$

$[C_2H_4][H_2O] = 0.80 \div 3.8 = 0.21$
$[C_2H_4] = [H_2O] = \sqrt{0.21} =$ **0.46 mol dm^{-3}**

Q2 a) $K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$

b) $K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{0.360^2}{(0.250)^2(0.180)} = 11.5$

units of $K_c = \frac{(\text{mol dm}^{-3})^2}{(\text{mol dm}^{-3})^2(\text{mol dm}^{-3})} = \frac{1}{(\text{mol dm}^{-3})}$

K_c = **11.5 mol^{-1} dm^3**

c) $[SO_2]^2 = \frac{[SO_3]^2}{K_c \times [O_2]} = \frac{0.360^2}{15 \times 0.180} = 0.048$

$[SO_2] = \sqrt{0.048} =$ **0.22 mol dm^{-3}**

Q3 Initial moles of $Fe^{2+} = \frac{0.500 \times 250}{1000} = 0.125$ mol

No. of moles of Fe^{2+} at equilibrium

$= \frac{0.0844 \times 500}{1000} = 0.0422$ mol

No. of moles of Fe^{3+} at equilibrium
= No. of moles of Fe^{2+} lost = 0.125 – 0.0422 = 0.0828 mol
So at equilibrium,
$[Ag^+] = [Fe^{2+}] = 0.0844$ mol dm^{-3}

$[Fe^{3+}] = \frac{0.0828 \times 1000}{500} = 0.1656$ mol dm^{-3}

You don't need to work out the number of moles of $Ag_{(s)}$ at equilibrium as solid products are not included in K_c.

So $K_c = \frac{[Fe^{3+}]}{[Fe^{2+}][Ag^+]} = \frac{0.1656}{0.0844 \times 0.0844} = 23.2$

units of $K_c = \frac{(\text{mol dm}^{-3})}{(\text{mol dm}^{-3})^2} = \frac{1}{(\text{mol dm}^{-3})} = \text{mol}^{-1}\text{ dm}^3$

K_c = **23.2 mol^{-1} dm^3**

Page 326 — Fact Recall Questions

Q1 A dynamic equilibrium occurs when a reversible reaction is still happening but the forward and backward reaction are going at exactly the same rate so there is no overall change in the concentrations of the reagents.

Q2 For a dynamic equilibrium to be established it must be a closed system and the temperature must be constant.

Q3 $K_c = \frac{[D]^d[E]^e}{[A]^a[B]^b}$

Q4 The units of K_c change depending on the concentration terms in the reaction.

2. Gas Equilibria

Page 330 — Application Questions

Q1 a) $2NH_{3(g)} + 1\frac{1}{2}O_{2(g)} \rightleftharpoons N_{2(g)} + 3H_2O_{(g)}$

b) total pressure = $p(NH_3) + p(O_2) + p(N_2) + p(H_2O)$

c) total pressure = 42 + 85 + 21 + 12 = **160 kPa**

d) mole fraction of gas in a mixture = number of moles of gas ÷ total number of moles of gas in a mixture
So mole fraction of H_2O = 12 ÷ 160 = **0.075**

Q2 No. moles of He = 4.00 ÷ 4 = 1.00
No. moles of O_2 = 2.81 ÷ (16 × 2) = 0.0878...
Total moles of gas = 1.00 + 0.0878... = 1.0878...
Mole fraction of O_2 = 0.0878... ÷ 1.0878... = 0.0807...
So partial pressure of O_2 = 0.0807... × 8.12
= **0.655 kPa (3 s.f.)**

Q3 a) $K_p = \frac{p(C_6H_{12})}{p(C_6H_6) \times p(H_2)^3}$

b) Since the partial pressures of all three gases are equal,
$p(C_6H_{12}) = p(C_6H_6) = p(H_2) = x$

$4.80 \times 10^{-13} = \frac{x}{x \times (x)^3} = \frac{1}{x^3}$

$x^3 = \frac{1}{4.80 \times 10^{-13}} = 2.083... \times 10^{12}$

$x = \sqrt[3]{2.083... \times 10^{12}}$

x = **12 800 kPa**

Q4 a) $2HF \rightleftharpoons H_2 + F_2$
Equal amounts of H_2 and F_2 are produced, so if there are 9.340 moles of F_2 present at equilibrium, there are also 9.340 moles of H_2.
Since 2 moles of HF produce 2 moles of product gases, the total number of moles of gas at equilibrium will be 24.32.
Mole fraction of H_2 = 9.340 ÷ 24.32 = 0.384...
Partial pressure of H_2 = 0.384... × 2313 = **888.3 kPa**

b) partial pressure of H_2 = partial pressure of F_2, so partial pressure of F_2 = 888.3 kPa.
$p(HF)$ = 2313 – 888.3 – 888.3 = 536.4 kPa

$K_p = \frac{p(H_2) \times p(F_2)}{p(HF)^2} = 888.3 \times 888.3 \div (536.4)^2 = 2.742$

units of $K_p = \frac{(\text{kPa})^2}{(\text{kPa})^2}$ = no units

So K_p = **2.742**

Page 330 — Fact Recall Questions

Q1 The partial pressure of a gas is the individual pressure that it exerts on a system.

Q2 mole fraction of a gas = number of moles of that gas ÷ total number of moles of gas in the mixture

Q3 The equilibrium constant for a reversible reaction where some, or all, of the reactants and products are gases.

Q4 $K_p = \frac{p(D)^d p(E)^e}{p(A)^a p(B)^b}$

3. Changing the Equilibrium

Page 333 — Application Questions

Q1 a) No effect — if the concentration of C_2F_4 increases the equilibrium will shift to counteract the change and K_c will stay the same.

b) The reaction is endothermic in the forward direction so increasing the temperature will shift the equilibrium to the right. As a result more product will be produced, so K_c will increase.

c) No effect — catalysts only affect the time taken to reach equilibrium and not the position of the equilibrium itself.

It's only changing temperature that changes the value of K_c.

Q2 a) Exothermic. If decreasing the temperature increases K_c then it must increase the amount of product formed. The equilibrium must have shifted to the right, so the forward reaction must be exothermic.

b) (i) The equilibrium would shift to the left.

(ii) The value of K_p would not change.

Q3 a) Increase the temperature.

b) E.g. decrease the pressure / increase the concentration of the reactants.

Page 334 — Fact Recall Questions

Q1 If there's a change in concentration, pressure or temperature then an equilibrium will move to help counteract the change.

Q2 a) It will increase K_c.

b) It will decrease K_c.

Q3 If the concentration of a reagent is changed the equilibrium will shift and the concentrations of other reagents will also change. So K_c will stay the same.

Q4 Increasing the pressure has no affect on the value of K_p.

Q5 Adding a catalyst doesn't change the position of the equilibrium or K_c, but it decreases the time taken to reach equilibrium.

Exam-style Questions — page 335

1 D ***(1 mark)***

2 a) (i) $K_c = \dfrac{[CO_2][H_2]^4}{[CH_4][H_2O]^2}$ ***(1 mark)***.

(ii) $K_c = (0.200 \times (0.280)^4) \div (0.0800 \times (0.320)^2) = 0.150$

$K_c = (\text{mol dm}^{-3} \times (\text{mol dm}^{-3})^4) \div (\text{mol dm}^{-3} \times (\text{mol dm}^{-3})^2) = \text{mol}^2\ \text{dm}^{-6}$ so $K_c = \mathbf{0.150\ mol^2\ dm^{-6}}$

(2 marks for correct answer, otherwise 1 mark for correct substitution of values into the expression from part (i).)

b) (i) $[CH_4] = \dfrac{[CO_2][H_2]^4}{K_c \times [H_2O]^2}$

$= (0.420 \times 0.480^4) \div (0.0800 \times 0.560^2)$

$= \mathbf{0.889\ mol\ dm^{-3}}$

(2 marks for correct answer, otherwise 1 mark for correct equation.)

(ii) Lower ***(1 mark)***. K_c is lower at temperature Z than at temperature Y. This means temperature Z has caused the equilibrium to shift to the left ***(1 mark)***. As the reaction is endothermic in the forward direction, the temperature must be lowered to make it shift in the exothermic direction ***(1 mark)***.

c) The value of K_c would not change ***(1 mark)***. Catalysts do not affect the position of the equilibrium, only the time taken to reach equilibrium ***(1 mark)***.

Section 3 — Acids, Bases and pH

1. Acids and Bases

Page 340 — Application Questions

Q1 a) Full: $2HCl_{(aq)} + 2Na_{(s)} \rightarrow 2NaCl_{(aq)} + H_{2(g)}$

Ionic: $2H^+_{(aq)} + 2Na_{(s)} \rightarrow 2Na^+_{(aq)} + H_{2(g)}$

Make sure you always include the H^+ ions in your ionic equations.

b) Full: $H_2SO_{4(aq)} + CaCO_{3(s)} \rightarrow CaSO_{4(aq)} + H_2O_{(l)} + CO_{2(g)}$

Ionic: $2H^+_{(aq)} + CO_3^{2-}{}_{(s)} \rightarrow H_2O_{(l)} + CO_{2(g)}$

c) Full: $HNO_{3(aq)} + KOH_{(aq)} \rightarrow KNO_{3(aq)} + H_2O_{(l)}$

Ionic: $H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)}$

d) Full: $2HCN_{(aq)} + Na_2O_{(s)} \rightarrow 2NaCN_{(aq)} + H_2O_{(l)}$

Ionic: $2H^+_{(aq)} + Na_2O_{(s)} \rightarrow H_2O_{(l)} + 2Na^+_{(aq)}$

Q2 a) $H_2CO_{3(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + HCO_3^-{}_{(aq)}$

acid 1 base 2 acid 2 base 1

b) $CH_3NH_{2(aq)} + H_2O_{(l)} \rightleftharpoons CH_3NH_3^+ + OH^-$

base 1 acid 2 acid 1 base 2

c) $CH_3COO^-_{(aq)} + NH_4^+{}_{(aq)} \rightleftharpoons CH_3COOH_{(aq)} + NH_{3(aq)}$

base 1 acid 2 acid 1 base 2

d) $HCl_{(aq)} + OH^-_{(aq)} \rightleftharpoons Cl^-_{(aq)} + H_2O_{(l)}$

acid 1 base 2 base 1 acid 2

Page 340 — Fact Recall Questions

Q1 a) A Brønsted-Lowry acid is a proton donor.

b) A Brønsted-Lowry base is a proton acceptor.

Q2 a) An acid that can only release one proton per molecule into solution, for example, HCl.

Other monobasic acids you could have mentioned include HNO_3, HBr and CH_3COOH.

b) An acid that can release two protons per molecule into solution, for example, H_2SO_4.

Other dibasic acids you could have mentioned include H_2CO_3 and H_2SO_3.

c) An acid that can release three protons per molecule into solution, for example, H_3PO_4.

Another tribasic acid you could have mentioned is citric acid ($C_6H_8O_7$).

Q3 a) A strong acid.

b) A weak base.

Q4 A conjugate pair is a set of two species that can be transformed into each other by gaining or losing a proton.

Q5 a) hydrogen gas and a salt

b) carbon dioxide, water and a salt

c) water and a salt

2. pH Calculations

Page 341 — Application Questions

Q1 $pH = -\log_{10} [H^+] = -\log_{10} [0.05] = \mathbf{1.3}$

Q2 $[H^+] = 10^{-pH} = 10^{-2.86} = \mathbf{1.4 \times 10^{-3}\ mol\ dm^{-3}}$

Q3 $pH = -\log_{10} [H^+] = -\log_{10} [0.02] = \mathbf{1.7}$

Page 342 — Application Questions

Q1 HCl is monobasic so $[H^+] = [HCl] = 0.08\ \text{mol dm}^{-3}$

$pH = -\log_{10} [H^+] = -\log_{10} [0.08] = \mathbf{1.1}$

Q2 HNO_3 is monobasic so $[H^+] = [HNO_3] = 0.12\ \text{mol dm}^{-3}$

$pH = -\log_{10} [H^+] = -\log_{10} [0.12] = \mathbf{0.92}$

Q3 $[H^+] = 10^{-pH} = 10^{-0.96} = 0.11\ \text{mol dm}^{-3}$

HCl is monobasic so $[HCl] = [H^+] = \mathbf{0.11\ mol\ dm^{-3}}$

Q4 $[H^+] = 10^{-pH} = 10^{-1.28} = 0.052\ \text{mol dm}^{-3}$

HNO_3 is monobasic so $[HNO_3] = [H^+] = \mathbf{0.052\ mol\ dm^{-3}}$

Page 342 — Fact Recall Questions

Q1 $pH = -\log_{10} [H^+]$

Q2 $[H^+] = 10^{-pH}$

Q3 Monobasic means that each molecule of acid releases one proton.

Q4 For strong monobasic acids the concentration of H^+ ions is the same as the concentration of the acid.

3. The Ionic Product of Water

Page 344 — Application Questions

Q1 For pure water $[H^+] = [OH^-]$ so $K_w = [H^+]^2$.
$[H^+] = \sqrt{K_w} = \sqrt{1.47 \times 10^{-14}} = 1.21... \times 10^{-7}$
$pH = -\log_{10} [H^+] = -\log_{10} (1.21... \times 10^{-7}) = \mathbf{6.916}$

Q2 For pure water $[H^+] = [OH^-]$ so $K_w = [H^+]^2$.
$[H^+] = \sqrt{K_w} = \sqrt{2.92 \times 10^{-14}} = 1.70... \times 10^{-7}$
$pH = -\log_{10} [H^+] = -\log_{10} (1.70... \times 10^{-7}) = \mathbf{6.767}$

Page 345 — Application Questions

Q1 KOH is a strong base so $[OH^-] = [KOH] = 0.200\ mol\ dm^{-3}$
$K_w = [H^+][OH^-]$ so $[H^+] = K_w \div [OH^-]$
$= (5.48 \times 10^{-14}) \div 0.200 = 2.74 \times 10^{-13}$
$pH = -\log_{10} [H^+] = -\log(2.74 \times 10^{-13}) = \mathbf{12.562}$

Q2 NaOH is a strong base so $[OH^-] = [KOH] = 0.155\ mol\ dm^{-3}$
$K_w = [H^+][OH^-]$ so $[H^+] = K_w \div [OH^-]$
$= (6.81 \times 10^{-15}) \div 0.155 = 4.39... \times 10^{-14}$
$pH = -\log_{10} [H^+] = -\log_{10} (4.39... \times 10^{-14}) = \mathbf{13.357}$

Q3 KOH is a strong base so $[OH^-] = [KOH] = 0.0840\ mol\ dm^{-3}$
$K_w = [H^+][OH^-]$ so $[H^+] = K_w \div [OH^-]$
$= (2.93 \times 10^{-15}) \div 0.0840 = 3.48... \times 10^{-14}$
$pH = -\log_{10} [H^+] = -\log_{10} (3.48... \times 10^{-14}) = \mathbf{13.457}$

Q4 $[H^+] = 10^{-pH} = 10^{-12.40} = 3.981... \times 10^{-13}\ mol\ dm^{-3}$
$K_w = [H^+][OH^-]$ so $[OH^-] = K_w \div [H^+]$
$= (6.8 \times 10^{-15}) \div (3.981... \times 10^{-13}) = 0.017\ mol\ dm^{-3}$
KOH is a strong base so $[KOH] = [OH^-] = \mathbf{0.017\ mol\ dm^{-3}}$

Q5 $[H^+] = 10^{-pH} = 10^{-13.98} = 1.047... \times 10^{-14}\ mol\ dm^{-3}$
$K_w = [H^+][OH^-]$ so $[OH^-] = K_w \div [H^+]$
$= (2.92 \times 10^{-14}) \div (1.047... \times 10^{-14}) = 2.79...\ mol\ dm^{-3}$
NaOH is a strong base so $[NaOH] = [OH^-] = \mathbf{2.8\ mol\ dm^{-3}}$

Q6 $[H^+] = 10^{-pH} = 10^{-13.25} = 5.623... \times 10^{-14}\ mol\ dm^{-3}$
$K_w = [H^+][OH^-]$ so $[OH^-] = K_w \div [H^+]$
$= (1.47 \times 10^{-14}) \div (5.623... \times 10^{-14}) = 0.261...\ mol\ dm^{-3}$
KOH is a strong base so $[KOH] = [OH^-] = \mathbf{0.26\ mol\ dm^{-3}}$

Page 345 — Fact Recall Questions

Q1 $K_w = [H^+][OH^-]$
For this question you can't put $K_w = [H^+]^2$ because this only applies to pure water.

Q2 $mol^2\ dm^{-6}$

Q3 In pure water, $[H^+] = [OH^-]$ so $K_w = [H^+]^2$.

4. The Acid Dissociation Constant

Page 349 — Application Questions

Q1 a) $K_a = [H^+][CN^-] \div [HCN]$ or $K_a = [H^+]^2 \div [HCN]$
b) $K_a = [H^+]^2 \div [HCN]$ so $[H^+]^2 = K_a \times [HCN]$
$= (4.9 \times 10^{-10}) \times 2.0 = 9.8 \times 10^{-10}$
$[H^+] = \sqrt{9.8 \times 10^{-10}} = 3.1... \times 10^{-5}\ mol\ dm^{-3}$
$pH = -\log_{10} [H^+] = -\log_{10} [3.1... \times 10^{-5}] = \mathbf{4.50}$

Q2 $[H^+] = 10^{-pH} = 10^{-3.80} = 1.5... \times 10^{-4}\ mol\ dm^{-3}$
$K_a = [H^+]^2 \div [HNO_2]$ so $[HNO_2] = [H^+]^2 \div K_a$
$= (1.5... \times 10^{-4})^2 \div 4.0 \times 10^{-4} = \mathbf{6.3 \times 10^{-5}\ mol\ dm^{-3}}$

Q3 $[H^+] = 10^{-pH} = 10^{-4.11} = 7.7... \times 10^{-5}\ mol\ dm^{-3}$
$K_a = [H^+]^2 \div [HA] = (7.7... \times 10^{-5})^2 \div 0.280$
$= \mathbf{2.2 \times 10^{-8}\ mol\ dm^{-3}}$

Q4 $[H^+] = 10^{-pH} = 10^{-3.67} = 2.1... \times 10^{-4}\ mol\ dm^{-3}$
$K_a = [H^+]^2 \div [HCOOH]$ so $[HCOOH] = [H^+]^2 \div K_a$
$= (2.1... \times 10^{-4})^2 \div (1.8 \times 10^{-4}) = \mathbf{2.5 \times 10^{-4}\ mol\ dm^{-3}}$

Q5 $K_a = 10^{-pKa} = 10^{-4.78} = \mathbf{1.6 \times 10^{-5}\ mol\ dm^{-3}}$

Q6 $[H^+] = 10^{-pH} = 10^{-4.50} = 3.1... \times 10^{-5}\ mol\ dm^{-3}$
$K_a = [H^+]^2 \div [HA] = (3.1... \times 10^{-5})^2 \div 0.154$
$= 6.4... \times 10^{-9}\ mol\ dm^{-3}$
$pK_a = -\log_{10} (K_a) = -\log_{10} (6.4... \times 10^{-9}) = \mathbf{8.19}$

Q7 $K_a = 10^{-pKa} = 10^{-3.14} = 7.24 \times 10^{-4}\ mol\ dm^{-3}$
$[H^+] = 10^{-pH} = 10^{-3.20} = 6.31 \times 10^{-4}\ mol\ dm^{-3}$
$K_a = [H^+]^2 \div [HF]$ so $[HF] = [H^+]^2 \div K_a$
$= (6.31 \times 10^{-4})^2 \div 7.24 \times 10^{-4} = \mathbf{5.5 \times 10^{-4}\ mol\ dm^{-3}}$

Q8 $K_a = 10^{-pKa} = 10^{-4.50} = 3.1... \times 10^{-5}\ mol\ dm^{-3}$
$K_a = [H^+]^2 \div [HX]$ so $[H^+]^2 = K_a \times [HX]$
$= (3.1... \times 10^{-5}) \times 0.60 = 1.8... \times 10^{-5}\ mol^2\ dm^{-6}$
so $[H^+] = \sqrt{1.8 \times 10^{-5}} = 4.3... \times 10^{-3}\ mol\ dm^{-3}$
$pH = -\log_{10} [H^+] = -\log_{10} [4.3... \times 10^{-3}] = \mathbf{2.36}$

Page 349 — Fact Recall Questions

Q1 $mol\ dm^{-3}$

Q2 a) $K_a = [H^+][A^-] \div [HA]$ or $K_a = [H^+]^2 \div [HA]$
b) $[HA] = [H^+][A^-] \div K_a$ or $[HA] = [H^+]^2 \div K_a$

Q3 a) $pK_a = -\log_{10}(K_a)$
b) $K_a = 10^{-pKa}$

5. Buffer Action

Page 352 — Fact Recall Questions

Q1 A buffer is a solution that minimises changes in pH when small amounts of acid or alkali are added.

Q2 By mixing a weak acid with a salt of its conjugate base, or by reacting an excess of a weak acid with a strong alkali.
When describing how to prepare a buffer from an acid and a base, make sure you say that the acid is in excess — you might lose a mark if you don't.

Q3 a) When acid is added $[H^+]$ increases. Most of the extra H^+ ions combine with A^- ions to form HA. This shifts the equilibrium to the left so $[H^+]$ is reduced to almost its original value and so the pH doesn't change much.
b) When a base is added $[OH^-]$ increases. Most of the extra OH^- ions react with H^+ ions to form water. This removes H^+ ions from the solution so the equilibrium shifts to the right and the HA dissociates to compensate. More H^+ ions are formed and so the pH doesn't change much.

Q4 A carbonic acid-hydrogencarbonate buffer system is used to buffer the pH of blood and keep it at 7.35 and 7.45.

6. Calculating the pH of Buffers

Page 355 — Application Questions

Q1 a) $CH_3CH_2COOH \rightleftharpoons H^+ + CH_3CH_2COO^-$ so

$$K_a = \frac{[H^+][CH_3CH_2COO^-]}{[CH_3CH_2COOH]}$$

b) $K_a = [H^+][CH_3CH_2COO^-] \div [CH_3CH_2COOH]$ so

$[H^+] = (K_a \times [CH_3CH_2COOH]) \div [CH_3CH_2COO^-]$

$= ((1.35 \times 10^{-5}) \times 0.200) \div 0.350 = \mathbf{7.71 \times 10^{-6}\ mol\ dm^{-3}}$

c) $pH = -\log_{10} [H^+] = -\log_{10} (7.71 \times 10^{-6}) = \mathbf{5.113}$

Q2 $CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$ so

$K_a = [H^+][CH_3COO^-] \div [CH_3COOH]$ so

$[H^+] = (K_a \times [CH_3COOH]) \div [CH_3COO^-]$

$= ((1.74 \times 10^{-5}) \times 0.150) \div 0.250 = 1.04... \times 10^{-5}$ mol dm^{-3}

$pH = -\log_{10} [H^+] = -\log_{10} (1.04... \times 10^{-5}) = \mathbf{4.981}$

Q3 a) $CH_3CH_2COOH + KOH \rightarrow CH_3CH_2COO^-K^+ + H_2O$

b) initial moles CH_3CH_2COOH = (conc. × vol.) ÷ 1000

= (0.500 × 30.0) ÷ 1000 = **0.0150 moles**.

initial moles KOH = (conc. × vol.) ÷ 1000

= (0.250 × 20.0) ÷ 1000 = $\mathbf{5.00 \times 10^{-3}}$ **moles**.

c) From the equation: moles of salt = moles of base

= 5.00×10^{-3} moles. Also, 1 mole of base neutralises 1 mole of acid so 5.00×10^{-3} moles of base neutralises 5.00×10^{-3} moles of acid.

So $0.0150 - (5.00 \times 10^{-3}) = 0.0100$ moles of acid remain.

Total volume = 30.0 + 20.0 = 50.0 cm^3

conc. acid in buffer = (moles × 1000) ÷ vol.

= (0.0100 × 1000) ÷ 50.0 = **0.200 mol dm^{-3}**

conc. salt in buffer = (moles × 1000) ÷ vol.

= $((5.00 \times 10^{-3}) \times 1000) \div 50.0$ = **0.100 mol dm^{-3}**

d) $K_a = [H^+][CH_3CH_2COO^-] \div [CH_3CH_2COOH]$ so

$[H^+] = (K_a \times [CH_3CH_2COOH]) \div [CH_3CH_2COO^-]$

$= ((1.35 \times 10^{-5}) \times 0.200) \div 0.100$

$= \mathbf{2.70 \times 10^{-5}\ mol\ dm^{-3}}$

e) $pH = -\log_{10} [H^+] = -\log_{10} (2.70 \times 10^{-5}) = \mathbf{4.569}$

Q4 initial moles HCOOH = (conc. × vol.) ÷ 1000

= $(0.200 \times 25.0) \div 1000 = 5.00 \times 10^{-3}$ moles.

initial moles NaOH = (conc. × vol.) ÷ 1000

= $(0.100 \times 15.0) \div 1000 = 1.50 \times 10^{-3}$ moles.

$HCOOH + NaOH \rightarrow HCOO^-Na^+ + H_2O$ so

moles of salt = moles of base = 1.50×10^{-3} moles. Also, 1 mole of base neutralises 1 mole of acid so 1.50×10^{-3} moles of base neutralises 1.50×10^{-3} moles of acid.

So $(5.00 \times 10^{-3}) - (1.50 \times 10^{-3}) = 3.50 \times 10^{-3}$ moles of acid remain.

Total volume = 15.0 + 25.0 = 40.0 cm^3

final conc. acid = (moles × 1000) ÷ vol.

= $((3.50 \times 10^{-3}) \times 1000) \div 40.0 = 0.0875$ mol dm^{-3}

final conc. salt = (moles × 1000) ÷ vol.

= $((1.50 \times 10^{-3}) \times 1000) \div 40.0 = 0.0375$ mol dm^{-3}

$K_a = [H^+][HCOO^-] \div [HCOOH]$ so

$[H^+] = (K_a \times [HCOOH]) \div [HCOO^-]$

$= ((1.60 \times 10^{-4}) \times 0.0875) \div 0.0375$

$= 3.73... \times 10^{-4}$ mol dm^{-3}

$pH = -\log_{10} [H^+] = -\log_{10} (3.73 \times 10^{-4}) = \mathbf{3.428}$

7. pH Curves and Titrations

Page 359 — Application Questions

Q1 a) Strong base/weak acid, phenolphthalein/cresol purple

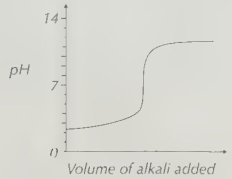
b) Strong acid/weak base, methyl orange

c) Strong acid/strong base, phenolphthalein/cresol purple/litmus

d) Weak base/strong acid, methyl orange

Q2 Any curve where the vertical section covers pH 6.8 to pH 8.0.

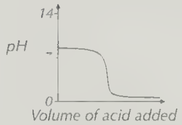
E.g.



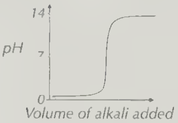
You could also have drawn a curve showing an acid being added to an alkali.

Page 360 — Fact Recall Questions

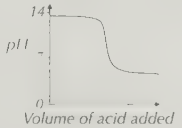
Q1 a)



b)



c)



If the question says that a strong acid neutralises a strong base, the base is being neutralised so it's the acid that's added.

Q2 a) At the end point of a titration a tiny amount of acid/base causes a sudden big change in pH and the base/acid is just neutralised.

b) The pH indicator changes colour/the pH meter shows a sudden big change.

c) The pH curve becomes close to vertical.

Q3 For an indicator to be suitable it must change colour over a narrow pH range that lies entirely within the vertical part of the pH curve for the titration.

Exam-style Questions — pages 361-362

1 B ***(1 mark)***

2 D ***(1 mark)***

3 a) (i) $HCOOH \rightleftharpoons H^+ + HCOO^-$ ***(1 mark)***

(ii) $K_a = [H^+][HCOO^-] \div [HCOOH]$ or
$K_a = [H^+]^2 \div [HCOOH]$ ***(1 mark)***

(iii) $[H^+] = 10^{-pH} = 10^{-2.18} = 6.6... \times 10^{-3}$
$K_a = [H^+]^2 \div [HCOOH] = (6.6... \times 10^{-3})^2 \div 0.240$
$= 1.8... \times 10^{-4}$ mol dm^{-3}
$pK_a = -\log_{10}(K_a) = -\log_{10}(1.8... \times 10^{-4}) = \mathbf{3.74}$
(3 marks for correct answer, otherwise 1 mark for $[H^+] = 6.6... \times 10^{-3}$ and 1 mark for $K_a = 1.8... \times 10^{-4}$.)

b) (i) $K_a = [H^+][HCOO^-] \div [HCOOH]$ so
$[H^+] = (K_a \times [HCOOH]) \div [HCOO^-]$
$= ((1.8 \times 10^{-4}) \times 0.084) \div (0.060)$
$= 2.5... \times 10^{-4}$ mol dm^{-3} ***(1 mark)***
$pH = -\log_{10}[H^+] = -\log_{10}(2.5... \times 10^{-4}) = \mathbf{3.60}$
(1 mark).

You calculated K_a for this acid in a previous part of the question. If you got it wrong then, you could still get full marks for this part of the question if everything else you did was right.

(ii) $HCOOH + NH_3 \rightarrow HCOO^- + NH_4^+$ ***(1 mark)***.
acid 1 base 2 base 1 acid 2
(1 mark for correctly identifying acids and bases, 1 mark for correct pairings.)

(iii) $HCOOH \rightleftharpoons H^+ + HCOO^-$. Adding an acid increases $[H^+]$ ***(1 mark)***. The excess H^+ combines with $HCOO^-$ to form HCOOH ***(1 mark)***, so the equilibrium shifts to the left reducing the H^+ concentration to close to its original value and maintaining the pH ***(1 mark)***.

4 a) (i) $K_w = [H^+][OH^-]$ ***(1 mark)***

(ii) $pH = -\log_{10}[H^+]$ ***(1 mark)***

b) NaOH is a strong base so
$[OH^-] = [NaOH] = 0.150$ mol dm^{-3}
$K_w = [H^+][OH^-]$ so $[H^+] = K_w \div [OH^-]$
$= (1.00 \times 10^{-14}) \div 0.150 = 6.66... \times 10^{-14}$ mol dm^{-3}
$pH = -\log_{10}[H^+] = -\log_{10}[6.66... \times 10^{-14}] = \mathbf{13.176}$
(3 marks for correct answer, otherwise 1 mark for $[OH^-] = 0.150$ and 1 mark for $[H^+] = 6.66... \times 10^{-4}$.)

c) (i) B ***(1 mark)***

This titration was a strong acid against a strong base so the curve should start at around pH 14 and fall to around pH 1.

(ii) HCl is a strong acid and fully dissociates so
$[H^+] = [HCl] = 0.203$ mol dm^{-3}
$pH = -\log_{10}[H^+] = -\log_{10}(0.203) = \mathbf{0.693}$
(2 marks for correct answer, otherwise 1 mark for $[H^+] = 0.203$ mol dm^{-3}.)

d) (i) Any weak acid (e.g. methanoic acid/ethanoic acid/hydrogen cyanide) ***(1 mark)***. Any strong base (e.g. potassium hydroxide/sodium hydroxide) ***(1 mark)***.

(ii) Phenolphthalein ***(1 mark)***

Section 4 — Enthalpy, Entropy and Free Energy

1. Enthalpy Changes

Page 364 — Fact Recall Questions

Q1 Enthalpy change is the heat energy transferred in a reaction at constant pressure.

Q2 ΔH

Q3 a) Enthalpy change of formation is the enthalpy change when 1 mole of a compound is formed from its elements.

b) Second electron affinity is the energy needed to change 1 mole of gaseous 1– ions into 1 mole of gaseous 2– ions.

c) The enthalpy change of hydration is the enthalpy change when 1 mole of gaseous ions is dissolved in water.

Q4 a) Enthalpy change of atomisation of an element.

b) The first ionisation energy.

Q5 a) $\Delta_{hyd}H$

b) $\Delta_{sol}H$

2. Lattice Enthalpy

Page 366 — Application Questions

Q1 a) Larger ions attract less strongly because their charge density is lower. So the larger the ionic radii of the ions involved, the less exothermic the lattice enthalpy. The ionic radii increase from Cl^- to I^-, so the lattice enthalpy becomes less exothermic from NaCl to NaI.

b) NaCl contains the strongest ionic bonds.

Q2 The standard lattice enthalpy of CaO would be more negative than the standard lattice enthalpy of K_2O. This is because CaO only contains 2+ ions while K_2O contains 1+ ions. The higher the charge on the ions, the more energy is released when the ionic lattice forms and the more negative the lattice enthalpy will be.

Page 366 — Fact Recall Questions

Q1 a) The lattice enthalpy is the enthalpy change when 1 mole of a solid ionic compound is formed from its gaseous ions.

b) $\Delta_{LE}H$

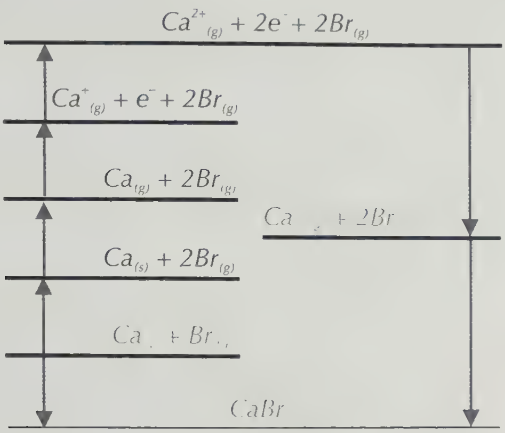
Q2 The more negative the lattice enthalpy, the stronger the ionic bonding in the lattice.

Q3 Ionic charge and ionic radius.

3. Born-Haber Cycles

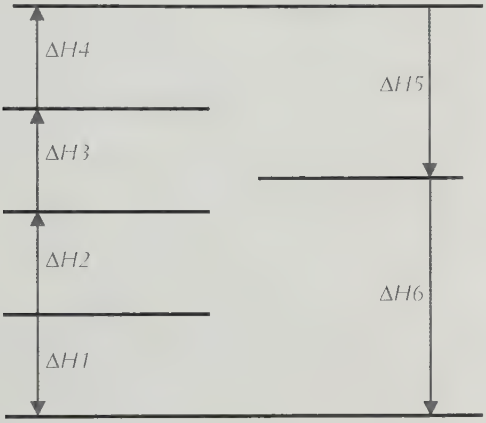
Page 370 — Application Questions

Q1 E.g.



$Ca^{2+}_{(g)} + 2e^- + 2Br_{(g)}$
$Ca^+_{(g)} + e^- + 2Br_{(g)}$
$Ca_{(g)} + 2Br_{(g)}$
Ca + 2Br
$Ca_{(s)} + 2Br_{(g)}$
Ca + Br
CaBr

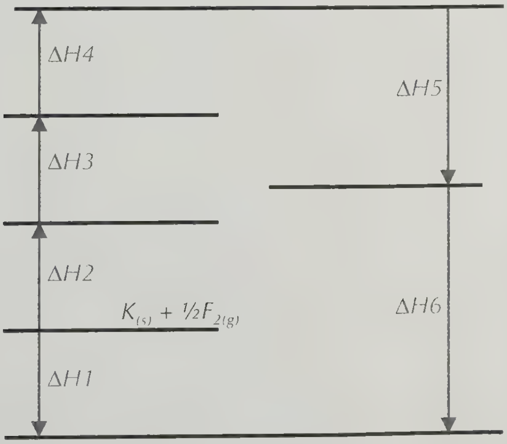
Q2 a) E.g.



ΔH4
ΔH5
ΔH3
ΔH2
ΔH6
ΔH1

b) $\Delta H1 = \Delta H2 + \Delta H3 + \Delta H4 + \Delta H5 + \Delta H6$
$= (+122) + (+159) + (+520) + (-349) + (-861)$
$=$ **-409 kJ mol^{-1}**

Q3 a) E.g.



ΔH4
ΔH5
ΔH3
ΔH2
$K_{(s)} + \frac{1}{2}F_{2(g)}$
ΔH6
ΔH1

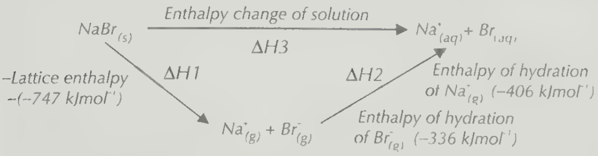
b) $\Delta H6 = -\Delta H5 - \Delta H4 - \Delta H3 - \Delta H2 + \Delta H1$
$= -(-328) - (+419) - (+89) - (+79) + (-563)$
$=$ **-822 kJ mol^{-1}**

4. Enthalpies of Solution

Page 374 — Application Questions

Q1 $\Delta H3 = \Delta H1 + \Delta H2 = -(-861) + (-520 + -364) =$ **-23 kJ mol^{-1}**

Q2 a)



Enthalpy change of solution
$NaBr_{(s)}$
$Na^+_{(aq)} + Br^-_{(aq)}$
ΔH3
–Lattice enthalpy –(–747 kJmol⁻¹)
ΔH1
ΔH2
Enthalpy of hydration of $Na^+_{(g)}$ (–406 kJmol⁻¹)
$Na^+_{(g)} + Br^-_{(g)}$
Enthalpy of hydration of $Br^-_{(g)}$ (–336 kJmol⁻¹)

b) $\Delta H3 = \Delta H1 + \Delta H2 = -(-747) + (-406 + -336)$
$=$ **$+5$ kJ mol^{-1}**

Q3 a) $\Delta H3 = \Delta H1 + \Delta H2 = -(-807) + (-520 + -336)$
$=$ **-49 kJ mol^{-1}**

b) $\Delta H3 = \Delta H1 + \Delta H2 = -(-701) + (-322 + -364)$
$=$ **$+15$ kJ mol^{-1}**

c) $\Delta H3 = \Delta H1 + \Delta H2 = -(-2440) + (-1921 + (-336 \times 2))$
$=$ **-153 kJ mol^{-1}**

Q4 Magnesium ions (Mg^{2+}) are smaller and have a higher charge than potassium ions (K^+). The higher charge and smaller size create a higher charge density. This creates a stronger attraction for the water molecules and gives magnesium ions a much more negative enthalpy of hydration than potassium ions.

Page 374 — Fact Recall Questions

Q1 a) The bonds between the ions break, and bonds between the ions and water are made.

b) Bonds breaking is endothermic and bonds being made is exothermic.

Q2 The lattice enthalpy and enthalpy change of hydration.

Q3 Ionic charge and ionic radius.

5. Entropy

Page 377 — Application Questions

Q1 The entropy will increase when the solid sodium hydroxide dissolves in the aqueous hydrogen chloride. The entropy of the water will increase when it turns to a gas and the entropy of the sodium chloride will decrease when it turns to a solid.

Q2 $\Delta S = S_{\text{products}} - S_{\text{reactants}}$
$= (214 + (2 \times 69.9)) - (186 + (2 \times 205))$
$=$ **-242 J K^{-1} mol^{-1}**

Q3 $\Delta S = S_{\text{products}} - S_{\text{reactants}}$
$= ((3 \times 31.6) + (2 \times 69.9)) - (248 + (2 \times 206))$
$=$ **-425 J K^{-1} mol^{-1}**

Page 377 — Fact Recall Questions

Q1 a) It is a measure of the amount of disorder in a system (e.g. the number of ways that particles can be arranged and the number of ways that the energy can be shared out between particles).

b) ΔS

Q2 a) The entropy increases because particles move around more in gases than in liquids and their arrangement is more disordered.

b) The entropy increases because particles move around more in solution than in solids and their arrangement is more disordered.

c) The entropy increases because the more gaseous particles you've got, the more ways they and their energy can be arranged.

6. Free Energy Change

Page 380 — Application Questions

Q1 a) $\Delta S = S_{products} - S_{reactants}$
$= ((2 \times 28.3) + (3 \times 27.0)) - (51.0 + (3 \times 32.5))$
$= \mathbf{-10.9\ J\ K^{-1}\ mol^{-1}}$

b) $\Delta H^{\circ} = -130\ kJ\ mol^{-1} = -130 \times 10^3\ J\ mol^{-1}$
$\Delta G = \Delta H - T\Delta S$
$= -130 \times 10^3 - (298 \times -10.9)$
$= \mathbf{-127\ 000\ J\ mol^{-1}}$ (3 s.f.)

c) The reaction is feasible at 298 K because ΔG is negative.

Q2 a) (i) $\Delta H^{\circ} = 71.0\ kJ\ mol^{-1} = 71.0 \times 10^3\ J\ mol^{-1}$
$\Delta G = \Delta H - T\Delta S$
$= 71.0 \times 10^3 - (298 \times 176)$
$= \mathbf{18\ 600\ J\ mol^{-1}}$ (3 s.f.)
The reaction is not feasible at 298 K because ΔG is positive.

(ii) $\Delta H^{\circ} = 71.0\ kJ\ mol^{-1} = 71.0 \times 10^3\ J\ mol^{-1}$
$\Delta G = \Delta H - T\Delta S$
$= (71.0 \times 10^3) - (600 \times 176)$
$= \mathbf{-34\ 600\ J\ mol^{-1}}$ (3 s.f.)
The reaction is feasible at 600 K because ΔG is negative.

b) $\Delta H^{\circ} = 71.0\ kJ\ mol^{-1} = (71.0 \times 10^3)\ J\ mol^{-1}$
$T = \Delta H \div \Delta S = (71.0 \times 10^3) \div 176 = \mathbf{403\ K}$ (3 s.f.)

Q3 $\Delta H^{\circ} = 178\ kJ\ mol^{-1} = 178 \times 10^3\ J\ mol^{-1}$
$T = \Delta H \div \Delta S = (178 \times 10^3) \div 165 = \mathbf{1080\ K}$ (3 s.f.)

Page 380 — Fact Recall Questions

Q1 a) Free energy change is a measure used to predict whether a reaction is feasible.

b) ΔG

Q2 $\Delta G = \Delta H - T\Delta S$

Q3 E.g. The reaction could have a very high activation energy / the rate of reaction might be so slow that you don't notice it happening.

Q4 no

Q5 $T = \Delta H \div \Delta S$

Exam-style Questions — pages 382-384

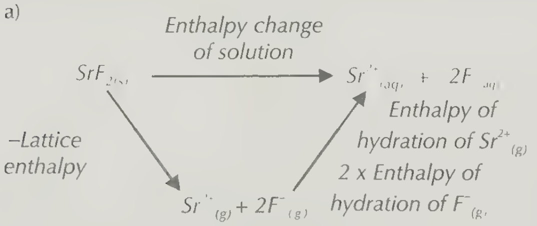
1 A ***(1 mark)***

Higher ionic charges result in more negative standard lattice enthalpies and smaller ionic radii result in more negative standard lattice enthalpies. B and C can be ruled out because Na, Cl, K and Br are all singly charged ions. D can be ruled out because Mg and S are larger ions than Be and O.

2 C ***(1 mark)***

According to the equation $\Delta G = \Delta H - T\Delta S$ for a reaction to be feasible at any temperature, ΔH must be negative and ΔS must be positive.

3 a)


Enthalpy change of solution
$SrF_{2(s)}$
$Sr^{2+}_{(aq)} + 2F^{-}_{(aq)}$
–Lattice enthalpy
Enthalpy of hydration of $Sr^{2+}_{(g)}$
2 x Enthalpy of hydration of $F^{-}_{(g)}$
$Sr^{2+}_{(g)} + 2F^{-}_{(g)}$

(1 mark for a complete correct cycle, 1 mark for correctly labelled arrows)

b) Enthalpy change of solution ($SrF_{2(s)}$)
= –lattice enthalpy ($SrF_{2(s)}$)
+ enthalpy of hydration ($Sr^{2+}_{(g)}$)
+ [2 × enthalpy of hydration ($F^{-}_{(g)}$)] ***(1 mark)***
$= -(-2492) + (-1480) + (2 \times -506) =$ **0 kJ mol⁻¹** ***(1 mark)***

You have to double the enthalpy of hydration for F^- because there are two in SrF_2.

4 a) Increase. 2 moles of solid reactant produce 1 mole of solid product and 1 mole of gaseous product. Gases have higher entropy than solids ***(1 mark)***.

b) $\Delta S = S_{products} - S_{reactants}$
$= (32.0 + 214) - (53.0 + 5.70)$
$= +187.3\ J\ K^{-1}\ mol^{-1}$ ***(1 mark)***.
$\Delta H^{\circ} = +127\ kJ\ mol^{-1} = +127 \times 10^3\ J\ mol^{-1}$
$\Delta G = \Delta H - T\Delta S$ ***(1 mark)***.
$= (+127 \times 10^3) - (1473 \times +187.3)$ ***(1 mark)***.
$= \mathbf{-149000\ J\ mol^{-1}}$ or $\mathbf{-149\ kJ\ mol^{-1}}$ (3 s.f.) ***(1 mark)***.

c) If the free energy change is negative or equal to zero the reaction is feasible ***(1 mark)***.

d) $T = \Delta H \div \Delta S$ ***(1 mark)***.

e) $T = (+127 \times 10^3) \div 187.3$
$= \mathbf{678\ K}$
(1 mark for correct substitution, 1 mark for correct answer).

Don't forget, reactions become feasible when ΔG is 0 J mol⁻¹.

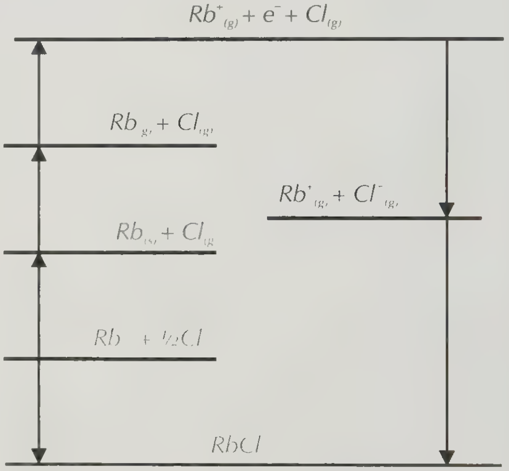
f) The enthalpy change of formation is the enthalpy change when 1 mole of a compound is formed from its elements ***(1 mark)***.

g) The formation of manganese(IV) oxide would be exothermic ***(1 mark)***.

It's an exothermic reaction because ΔH is negative.

5 a) It is the enthalpy change when 1 mole of a solid ionic lattice is formed from its gaseous ions ***(1 mark)***.

b)

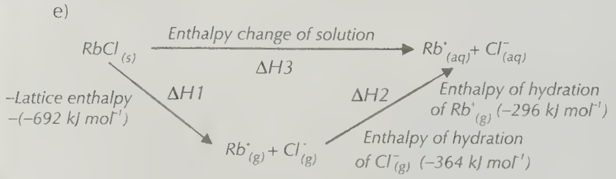

$Rb^{+}_{(g)} + e^{-} + Cl_{(g)}$
$Rb_{(g)} + Cl_{(g)}$
$Rb^{+}_{(g)} + Cl^{-}_{(g)}$
$Rb_{(s)} + Cl_{(g)}$
$Rb_{(s)} + \frac{1}{2}Cl_{2(g)}$
$RbCl$

(3 marks — 1 mark for each correct label).

c) $\Delta H6 = -\Delta H5 - \Delta H4 - \Delta H3 - \Delta H2 + \Delta H1$
$= -(-349) - (+403) - (+81) - (+122) + (-435)$
$= \mathbf{-692\ kJ\ mol^{-1}}$
(3 marks for correct answer, otherwise 1 mark for correct equation, 1 mark for correct substitution)

d) Sodium has a smaller ionic radius than rubidium ***(1 mark)***. Smaller ions have a higher charge density and attract more strongly ***(1 mark)***. So more energy is released when sodium chloride forms than when rubidium chloride forms ***(1 mark)***.

e)


Enthalpy change of solution
$RbCl_{(s)}$
$Rb^{+}_{(aq)} + Cl^{-}_{(aq)}$
$\Delta H3$
–Lattice enthalpy
–(–692 kJ mol⁻¹)
$\Delta H1$
$\Delta H2$
Enthalpy of hydration of $Rb^{+}_{(g)}$ (–296 kJ mol⁻¹)
$Rb^{+}_{(g)} + Cl^{-}_{(g)}$
Enthalpy of hydration of $Cl^{-}_{(g)}$ (–364 kJ mol⁻¹)

$\Delta H3 = \Delta H1 + \Delta H2 = -(-692) + (-296 + -364)$ ***(1 mark)***
$= \mathbf{+32\ kJ\ mol^{-1}}$ ***(1 mark)***

If you used the value of –300 kJ mol⁻¹ for the standard lattice enthalpy of rubidium chloride you'll get an answer of –360 kJ mol⁻¹. If you got this answer, give yourself full marks.

Section 5 — Redox and Electrode Potentials

1. Redox Reactions

Page 387 — Application Questions

Q1 $2Fe_{(s)} + 3Cu^{2+}_{(aq)} \rightarrow 2Fe^{3+}_{(aq)} + 3Cu_{(s)}$

Q2 $Cl_{2(g)} + 2e^- \rightarrow 2Cl^-_{(aq)}$

Q3 a) $Zn \rightarrow Zn^{2+} + 2e^-$

$Cr_2O_7^{2-} + 14H^+ + 6e \rightarrow 2Cr^{3+} + 7H_2O$

b) $Cr_2O_7^{2-} + 14H^+ + 3Zn \rightarrow 2Cr^{3+} + 3Zn^{2+} + 7H_2O$

Don't forget to finish off by double-checking that the charges on each side of the equation balance.

Q4 a) +6

b) $CH_3CH_2OH + H_2O \rightarrow CH_3COOH + 4H^+ + 4e^-$

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

c) $3CH_3CH_2OH + 2Cr_2O_7^{2-} + 16H^+$

$\rightarrow 3CH_3COOH + 4Cr^{3+} + 11H_2O$

Page 387 — Fact Recall Questions

Q1 a) Something that accepts electrons and gets reduced.

b) Something that donates electrons and gets oxidised.

Q2 It decreases.

2. Redox Titrations

Page 391 — Application Questions

Q1 a) $MnO_{4\ (aq)}^- + 8H^+_{(aq)} + 5Fe^{2+}_{(aq)} \rightarrow Mn^{2+}_{(aq)} + 4H_2O_{(l)} + 5Fe^{3+}_{(aq)}$

b) Moles Fe^{2+} = (conc. × volume) ÷ 1000

= (0.0500 × 28.2) ÷ 1000 = **1.41×10^{-3} moles**

c) From the balanced equation, 5 moles of Fe^{2+} reacts with 1 mole of MnO_4^- and so 1.41×10^{-3} moles of Fe^{2+} must react with $(1.41 \times 10^{-3}) \div 5$

$= 2.82 \times 10^{-4}$ moles of MnO_4^-.

Conc. MnO_4^- = (moles × 1000) ÷ volume

$= ((2.82 \times 10^{-4}) \times 1000) \div 30.0 =$ **9.40×10^{-3} mol dm^{-3}**

Q2 $MnO_{4\ (aq)}^- + 8H^+_{(aq)} + 5Fe^{2+}_{(aq)} \rightarrow Mn^{2+}_{(aq)} + 4H_2O_{(l)} + 5Fe^{3+}_{(aq)}$

Moles Fe^{2+} = (conc. × volume) ÷ 1000

= (0.600 × 28.0) ÷ 1000 = 0.0168 moles.

5 moles of Fe^{2+} reacts with 1 mole of MnO_4^- and so 0.0168 moles of Fe^{2+} must react with (0.0168) ÷ 5

$= 3.36 \times 10^{-3}$ moles of MnO_4^-.

Volume MnO_4^- = (moles × 1000) ÷ conc.

$= ((3.36 \times 10^{-3}) \times 1000) \div 0.0750 =$ **44.8 cm^3**

Q3 a) $Cr_2O_{7\ (aq)}^{2-} + 14H^+_{(aq)} + 6Fe^{2+}_{(aq)} \rightarrow 2Cr^{3+}_{(aq)} + 7H_2O_{(l)} + 6Fe^{3+}_{(aq)}$

b) Moles $Cr_2O_7^{2-}$ = (conc. × volume) ÷ 1000

= (0.150 × 22.2) ÷ 1000 = **3.33×10^{-3} moles**

c) From the balanced equation, 1 mole of $Cr_2O_7^{2-}$ reacts with 6 moles of Fe^{2+}, so 3.33×10^{-3} moles of $Cr_2O_7^{2-}$ must react with $(3.33 \times 10^{-3}) \times 6$

= 0.01998 moles of Fe^{2+}.

Conc. Fe^{2+} = (moles × 1000) ÷ volume

= (0.01998 × 1000) ÷ 20.0 = **0.999 mol dm^{-3}**

Q4 $Cr_2O_{7\ (aq)}^{2-} + 14H^+_{(aq)} + 6Fe^{2+}_{(aq)} \rightarrow 2Cr^{3+}_{(aq)} + 7H_2O_{(l)} + 6Fe^{3+}_{(aq)}$

Moles $Cr_2O_7^{2-}$ = (conc. × volume) ÷ 1000

$= (0.0550 \times 24.0) \div 1000 = 1.32 \times 10^{-3}$ moles.

1 mole of $Cr_2O_7^{2-}$ reacts with 6 moles of Fe^{2+}, so 1.32×10^{-3} moles of $Cr_2O_7^{2-}$ must react with $(1.32 \times 10^{-3}) \times 6 = 7.92 \times 10^{-3}$ moles of Fe^{2+}.

Volume Fe^{2+} = (moles × 1000) ÷ conc.

$= ((7.92 \times 10^{-3}) \times 1000) \div 0.450 =$ **17.6 cm^3**

Q5 a) $Cr_2O_{7\ (aq)}^{2-} + 14H^+_{(aq)} + 3Zn_{(s)} \rightarrow 2Cr^{3+}_{(aq)} + 7H_2O_{(l)} + 3Zn^{2+}_{(aq)}$

b) Moles $Cr_2O_7^{2-}$ = (conc. × volume) ÷ 1000

= (0.230 × 30.0) ÷ 1000 = **6.90×10^{-3} moles**

c) Using the balanced equation, 1 mole of $Cr_2O_7^{2-}$ reacts with 3 moles of Zn, so 6.90×10^{-3} moles of $Cr_2O_7^{2-}$ must react with (6.90×10^{-3} moles) × 3 = 0.0207 moles of Zn.

mass Zn = moles × M_r

= 0.0207 × 65.4 = **1.35 g**

Page 391 — Fact Recall Questions

Q1 E.g. Acidified potassium manganate(VII) solution/$KMnO_{4(aq)}$ / Acidified potassium dichromate(VI) solution/$K_2Cr_2O_{7(aq)}$.

Q2 Acid is added to make sure there are enough H^+ ions to allow all the oxidising agent to be reduced.

Q3 E.g. the end point is when the mixture in the flask just becomes tainted with the colour of the oxidising agent.

3. More on Titrations

Page 394 — Application Questions

Q1 a) Moles $Na_2S_2O_3$ = (conc. × volume) ÷ 1000

= (0.200 × 41.1) ÷ 1000 = **0.00822 moles**.

b) Using the balanced equation given in the question, 1 mole of I_2 reacts with 2 moles of $Na_2S_2O_3$ and so 0.00822 moles of $Na_2S_2O_3$ must react with 0.00822 ÷ 2 = **0.00411 moles** of I_2.

c) Using the balanced equation:

$IO_{3\ (aq)}^- + 5I^-_{(aq)} + 6H^+_{(aq)} \rightarrow 3I_{2\ (aq)} + 3H_2O_{(l)}$,

1 mole of IO_3^- will react to give 3 moles of I_2. So, 0.00411 moles of I_2 will be produced from 0.00411 ÷ 3 = **0.00137 moles** of IO_3^-.

d) Concentration of IO_3^- = (moles × 1000) ÷ volume

= (0.00137 × 1000) ÷ 13.2 = **0.104 mol dm^{-3}**

Q2 a) Moles $Na_2S_2O_3$ = (conc. × volume) ÷ 1000

= (0.750 × 4.00) ÷ 1000 = **0.00300 moles**.

b) Using the balanced equation given in the question, 2 moles of $Na_2S_2O_3$ react with 1 mole of I_2, and so 0.00300 moles of $Na_2S_2O_3$ must react with 0.00300 ÷ 2 = 0.00150 moles of I_2.

The total volume of the solution formed by adding the potassium manganate(VII) solution to the acidified potassium iodide solution was (39 + 61) = 100 cm^3. But only 25.0 cm^3 of the solution was used in the titration, so the total number of moles of I_2 formed in the oxidation reaction was 0.00150 × (100 ÷ 25)

= **0.00600 moles**.

c) Using the balanced equation given in the question, 5 moles of I_2 will be produced from 2 moles of MnO_4^-. So, 0.00600 moles of I_2 will be produced from (0.00600 ÷ 5) × 2 = 0.00240 moles of MnO_4^-.

Concentration of MnO_4^- = (moles × 1000) ÷ volume

= (0.00240 × 1000) ÷ 39.0 = **0.0615 mol dm^{-3}**

Q3 Moles $Na_2S_2O_3$ = (conc. × volume) ÷ 1000

$= (0.0600 \times 22.3) \div 1000 = (1.338 \times 10^{-3})$ moles.

Using the balanced equation given in the question, 1 mole of I_2 reacts with 2 moles of $Na_2S_2O_3$ and so 1.338×10^{-3} moles of $Na_2S_2O_3$ must react with $1.338 \times 10^{-3} \div 2$

$= 6.69 \times 10^{-4}$ moles of I_2.

Using the balanced equation given in the question, 1 mole of $Cr_2O_7^{2-}$ will produce 3 moles of I_2. So, 6.69×10^{-4} moles of I_2 will be produced from $(6.69 \times 10^{-4}) \div 3$

$= 2.23 \times 10^{-4}$ moles of $Cr_2O_7^{2-}$.

Concentration of $Cr_2O_7^{2-}$ = (moles × 1000) ÷ volume

$= ((2.23 \times 10^{-4}) \times 1000) \div 15.0 =$ **1.49×10^{-2} mol dm^{-3}**

Page 394 — Fact Recall Questions

Q1 $IO_{3\ (aq)}^- + 5I^-_{(aq)} + 6H^+_{(aq)} \rightarrow 3I_{2(aq)} + 3H_2O_{(l)}$

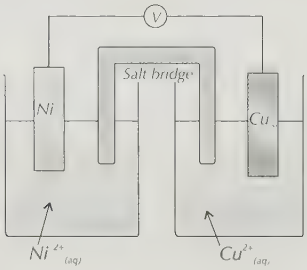
Q2 $I_{2\ (aq)} + 2S_2O_3{}^{2-}_{\ (aq)} \rightarrow 2I^-_{(aq)} + S_4O_6{}^{2-}_{\ (aq)}$

Q3 Put the flask containing the iodine solution under a burette. From the burette, add sodium thiosulfate solution to the flask drop by drop. When the iodine colour fades to a pale yellow, add 2 cm^3 of starch solution (to detect the presence of iodine). The solution in the conical flask will go dark blue, showing there's still some iodine there. Add sodium thiosulfate one drop at a time until the blue colour disappears. Record the volume of sodium thiosulfate added to the solution.

4. Electrochemical Cells

Pages 397-398 — Application Questions

Q1 a)



b) The Ni/Ni^{2+} reaction goes in the direction of oxidation (Ni is oxidised and Cu^{2+} is reduced).

You know that Ni is oxidised because the Ni/Ni^{2+} half-reaction has the more negative electrode potential.

Q2 a) $Ag^+_{(aq)} + e^- \rightarrow Ag_{(s)}$

b) $Ca_{(s)} \rightarrow Ca^{2+}_{(aq)} + 2e^-$

Q3 The Mg^{2+}/Mg half-cell.

Page 398 — Fact Recall Questions

Q1 a) platinum / graphite

b) Platinum/graphite is a solid that conducts electricity (so it will complete the circuit). It is also inert, so it won't react with the solutions in the half-cell.

Q2 a) It allows ions to flow between the half-cells and balance out the charges, completing the circuit.

b) The cell potential / the voltage between the two half-cells.

Q3 reduction

Q4 The metal that is very easy to oxidise.

5. Standard Electrode Potentials

Page 400 — Application Question

Q1 a) 1.00 mol dm^{-3}

All solutions being at 1.00 mol dm^{-3} is part of the definition of standard conditions.

b) –0.13 V

Page 400 — Fact Recall Questions

Q1 E.g. temperature, pressure and concentrations of reactants.

Q2 Hydrogen gas is bubbled into a solution of aqueous H$^+$ ions. The electrode is made of platinum foil. The standard conditions used are a temperature of 298 K (25 °C), a pressure of 100 kPa and all solutions of ions have a concentration of 1.00 mol dm^{-3}.

Q3 0.00 V

6. Electrochemical Series

Page 404 — Application Questions

Q1 a) $Al^{3+}_{(aq)} + 3e^- \rightleftharpoons Al_{(s)}$ $E^{\ominus} = -1.66\text{ V}$

$Ag^+_{(aq)} + e^- \rightleftharpoons Ag_{(s)}$ $E^{\ominus} = +0.80\text{ V}$

$E^{\ominus}_{cell} = E^{\ominus}_{reduced} - E^{\ominus}_{oxidised} = 0.80 - (-1.66)$

$= 2.46 = $ **+2.5 V (2 s.f.)**

b) $Cu^{2+}_{(aq)} + 2e^- \rightleftharpoons Cu_{(s)}$ $E^{\ominus} = +0.34\text{ V}$

$Cl_{2\ (g)} + 2e^- \rightleftharpoons 2Cl^-_{(aq)}$ $E^{\ominus} = +1.36$

$E^{\ominus}_{cell} = E^{\ominus}_{reduced} - E^{\ominus}_{oxidised} = 1.36 - 0.34$

$= 1.02 = $ **+1.0 V (2 s.f.)**

c) $Sn^{4+}_{(aq)} + 2e^- \rightleftharpoons Sn^{2+}_{(aq)}$ $E^{\ominus} = +0.15\text{ V}$

$Fe^{3+}_{(aq)} + e^- \rightleftharpoons Fe^{2+}_{(aq)}$ $E^{\ominus} = +0.77\text{ V}$

$E^{\ominus}_{cell} = E^{\ominus}_{reduced} - E^{\ominus}_{oxidised} = 0.77 - 0.15 = $ **+0.62 V (2 s.f.)**

Q2 a) $Mg^{2+}_{(aq)} + 2e^- \rightleftharpoons Mg_{(s)}$ $E^{\ominus} = -2.37\text{ V}$

$Ni^{2+}_{(aq)} + 2e^- \rightleftharpoons Ni_{(s)}$ $E^{\ominus} = -0.25\text{ V}$

Oxidation reaction: $Mg_{(s)} \rightarrow Mg^{2+}_{(aq)} + 2e^-$

Reduction reaction: $Ni^{2+}_{(aq)} + 2e^- \rightarrow Ni_{(s)}$

Redox reaction: $Mg_{(s)} + Ni^{2+}_{(aq)} \rightarrow Mg^{2+}_{(aq)} + Ni_{(s)}$

This matches the direction of the reaction given in the question, so this reaction is feasible.

b) $Fe^{3+}_{(aq)} + e^- \rightleftharpoons Fe^{2+}_{(aq)}$ $E^{\ominus} = +0.77\text{ V}$

$Br_{2\ (aq)} + 2e^- \rightleftharpoons 2Br^-_{(aq)}$ $E^{\ominus} = +1.09\text{ V}$

Oxidation reaction: $Fe^{2+}_{(aq)} \rightarrow Fe^{3+}_{(aq)} + e^-$

Reduction reaction: $Br_{2(l)} + 2e^- \rightarrow 2Br^-_{(aq)}$

Redox reaction: $2Fe^{2+}_{(aq)} + Br_{2\ (l)} \rightarrow 2Fe^{3+}_{(aq)} + 2Br^-_{(aq)}$

This does not match the direction of the reaction given in the question, so this reaction is not feasible.

c) $Sn^{4+}_{(aq)} + 2e^- \rightleftharpoons Sn^{2+}_{(aq)}$ $E^{\ominus} = +0.15\text{ V}$

$Cu^{2+}_{(aq)} + 2e^- \rightleftharpoons Cu_{(s)}$ $E^{\ominus} = +0.34\text{ V}$

Oxidation reaction: $Sn^{2+}_{(aq)} \rightarrow Sn^{4+}_{(aq)} + 2e^-$

Reduction reaction: $Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$

Redox reaction: $Sn^{2+}_{(aq)} + Cu^{2+}_{(aq)} \rightarrow Sn^{4+}_{(aq)} + Cu_{(s)}$

This matches the direction of the reaction given in the question, so this reaction is feasible.

Q3 $Sn^{4+}_{(aq)} + 2e^- \rightleftharpoons Sn^{2+}_{(aq)}$ $E^{\ominus} = +0.15$

$Ag^+_{(aq)} + e^- \rightleftharpoons Ag_{(s)}$ $E^{\ominus} = +0.80$

Oxidation reaction: $Sn^{2+}_{(aq)} \rightarrow Sn^{4+}_{(aq)} + 2e^-$

Reduction reaction: $Ag^+_{(aq)} + e^- \rightarrow Ag_{(s)}$

Redox reaction: $Sn^{2+}_{(aq)} + 2Ag^+_{(aq)} \rightarrow Sn^{4+}_{(aq)} + 2Ag_{(s)}$

This matches the direction of the reaction described in the question, so this reaction is feasible.

Page 404 — Fact Recall Questions

Q1 A list of electrode potentials for different electrochemical half-cells, written in order from the most negative to the most positive.

Q2 In the direction of reduction.

Q3 Reduction.

Q4 Any two from, e.g. the conditions are not standard / the reaction kinetics are not favourable / the activation energy may be too high / the rate of reaction may be too slow.

7. Energy Storage Cells

Page 406 — Application Questions

Q1 $2Ni(OH)_{2(s)} + Cd(OH)_{2(s)} \rightarrow 2NiOOH_{(s)} + Cd_{(s)} + 2H_2O_{(l)}$

Q2 a) $E^\ominus_{cell} = E^\ominus_{reduced} - E^\ominus_{oxidised} = 0.75 - (\ 0.76)$

$= 1.51 =$ **+1.5 V (2 s.f.)**

b) $2MnO_{2(s)} + 2NH_4{}^+{}_{(aq)} + Zn_{(s)}$

$\rightarrow Mn_2O_{3(s)} + 2NH_{3(aq)} + H_2O_{(l)} + Zn^{2+}{}_{(aq)}$

Q3 $PbSO_{4(s)} + 2e^- \rightleftharpoons Pb_{(s)} + SO_4{}^{2-}{}_{(aq)}$

$PbSO_{4(s)} + 2H_2O_{(l)} \rightleftharpoons PbO_{2(s)} + SO_4{}^{2-}{}_{(aq)} + 4H^+{}_{(aq)} + 2e^-$

Look at the half-cell half-equations given in the question. The top reaction has the more negative electrode potential. When the battery is discharging that one will go in the direction of oxidation and the bottom one will go in the direction of reduction. So when the battery is being recharged, the half-equations will go in the opposite directions.

Page 406 — Fact Recall Questions

Q1 battery

Q2 $E^\ominus_{cell} = E^\ominus_{reduced} - E^\ominus_{oxidised}$

Q3 Some energy storage cells can be recharged because the reactions that occur within them can be reversed if a current is supplied to force the electrons to flow in the opposite direction around the circuit.

8. Fuel Cells

Page 408 — Application Question

Q1 a) $CH_3OH + 1½O_2 \rightleftharpoons CO_2 + 2H_2O$

b) (i) $1½O_2 + 6H^+ + 6e^- \rightleftharpoons 3H_2O$

(ii) $CH_3OH + H_2O \rightleftharpoons CO_2 + 6H^+ + 6e^-$

c) $E^\ominus_{cell} = E^\ominus_{reduced} - E^\ominus_{oxidised}$

$= +1.23 - (+0.046) = 1.184 =$ **+1.2 V (2 s.f.)**

Page 408 — Fact Recall Questions

Q1 Fuel cells produce electricity by reacting a fuel with an oxidant.

Q2 At the anode, the platinum catalyst splits the H_2 into protons and electrons. The polymer electrolyte membrane (PEM) only allows the H^+ across. This forces the electrons to travel around the circuit to get to the cathode. At the cathode, O_2 combines with the H^+ from the anode and the electrons from the circuit to make H_2O. So an electric current is created in the circuit.

Exam-style Questions — pages 409-412

1 D ***(1 mark)***

If you use the electrochemical series to work out the feasible direction for these four reactions, you'll find that the only one where the direction doesn't match the question is D.

2 B ***(1 mark)***

The oxidation number of iron drops from +2 to 0.

3 B ***(1 mark)***

4 a) $2NiOOH_{(s)} + Zn_{(s)} + 2H_2O_{(l)} \rightarrow 2Ni(OH)_{2(s)} + Zn(OH)_{2(s)}$

(1 mark for correct reactants and products, 1 mark for balancing).

b) $E^\ominus_{cell} = E^\ominus_{reduced}\ \ E^\ominus_{oxidised}$ so

$E^\ominus_{reduced} = E^\ominus_{cell} + E^\ominus_{oxidised} = 1.73 + (-1.25) =$ **+0.480 V**

(2 marks for correct answer, otherwise 1 mark for correct substitution).

You know you're looking for $E_{reduced}$ because $Zn_{(s)}$ is being oxidised, so $NiOOH_{(s)}$ must be being reduced.

5 a) $4Li_{(s)} + 2SOCl_{2(aq)} \rightarrow 4LiCl_{(s)} + S_{(s)} + SO_{2(g)}$

(1 mark for correct reactants and products, 1 mark for balancing)

First you need to work out which half-equation will go in the oxidation direction and which in the reduction direction. Then write out the half-equation for the oxidation reaction the right way round. Finally, you can balance and combine them. What a lot of work for a measly two marks...

b) $E^\ominus_{cell} = E^\ominus_{reduced} - E^\ominus_{oxidised} = 0.47 - (-3.04)$

$= 3.51 =$ **3.5 V (2 s.f.)** ***(1 mark)***

c) Advantages: any one from, e.g. they are cheap to make / they have relatively high power densities / some types are rechargeable ***(1 mark)***.

Disadvantages: any one from, e.g. producing them involves using toxic chemicals which need to be disposed of safely / the chemical used to make the cells are often very flammable ***(1 mark)***.

6 a) (i) $E^\ominus$ for Sn^{4+}/Sn^{2+} is more negative than $E^\ominus$ for $VO_2{}^+/VO^{2+}$, so Sn^{2+} ions will react with $VO_2{}^+$ ions ***(1 mark)***.

$2VO_2{}^+{}_{(aq)} + Sn^{2+}{}_{(aq)} + 4H^+{}_{(aq)}$

$\rightarrow 2VO^{2+}{}_{(aq)} + Sn^{4+}{}_{(aq)} + 2H_2O_{(l)}$ ***(1 mark)***.

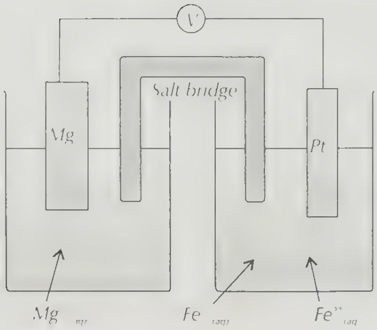
$E^\ominus$ for Sn^{4+}/Sn^{2+} is more negative than $E^\ominus$ for VO^{2+}/V^{3+}, so Sn^{2+} ions will react with VO^{2+} ions created in the previous reaction ***(1 mark)***.

$2VO^{2+}{}_{(aq)} + Sn^{2+}{}_{(aq)} + 4H^+{}_{(aq)} \rightarrow 2V^{3+} + Sn^{4+} + 2H_2O$ ***(1 mark)***.

The V^{3+} ions made in this reaction don't react with the Sn^{2+} ions because the electrode potential for V^{3+}/V^{2+} is more negative than that for Sn^{4+}/Sn^{2+}.

(ii) Any two from: e.g. the conditions may not be standard / the reaction kinetics may not be favourable/the rate of reaction may be too slow / the activation energy may be too high ***(1 mark for each, maximum 2 marks)***.

b) (i)



(1 mark for complete circuit with voltmeter and salt bridge, 1 mark for Mg/Mg^{2+} half-cell correct, 1 mark for Fe^{2+}/Fe^{3+} half-cell correct).

Don't forget to include the platinum electrode for the Fe^{2+}/Fe^{3+} half-cell.

(ii) $E_{cell} = E_{reduced} - E_{oxidised} = 0.77 - (-2.38)$
$= 3.15 =$ **3.2 V (2 s.f.)** ***(1 mark)***

(iii) $Mg_{(s)} + 2Fe^{3+} \rightarrow Mg^{2+}_{(aq)} + 2Fe^{2+}$ ***(1 mark for correct reactants and products, 1 mark for balancing)***

c) (i) A temperature of 298 K ***(1 mark)***. A pressure of 100 kPa ***(1 mark)***. Any solutions of ions have a concentration of 1.00 mol dm^{-3} ***(1 mark)***.

(ii) E.g. platinum is inert / platinum is a solid that conducts electricity ***(1 mark)***.

d) +0.80 V ***(1 mark)***.

7 a) $Li^+[CoO_2]^-_{(s)} \rightleftharpoons CoO_{2(s)} + Li_{(s)}$ ***(1 mark)***

b) The reactions that occur within them can be reversed if a current is supplied to force the electrons to flow in the opposite direction around the circuit ***(1 mark)***.

8 a) Place the flask containing the iodine solution produced by the reaction underneath a burette ***(1 mark)***. From the burette, add sodium thiosulfate solution to the flask drop by drop ***(1 mark)***. When the iodine colour fades to a pale yellow, add starch solution ***(1 mark)***. The solution in the conical flask will go dark blue, showing there's still some iodine there ***(1 mark)***. Add sodium thiosulfate one drop at a time until the blue colour disappears — this is the end point of the reaction ***(1 mark)***.

b) Moles $Na_2S_2O_3$ = (conc. × volume) ÷ 1000
= (0.500 × 23.6) ÷ 1000 = 0.0118 moles ***(1 mark)***.
Using the balanced equation given in the question, 1 mole of I_2 reacts with 2 moles of $Na_2S_2O_3$ and so 0.0118 moles of $Na_2S_2O_3$ must react with 0.0118 ÷ 2 = 0.0059 moles of I_2 ***(1 mark)***.
Using the balanced equation given in the question, 2 moles of Cu^{2+} will react to give 1 mole of I_2. So, 0.0059 moles of I_2 will be formed from 0.0059 × 2 = **0.0118 moles** of Cu^{2+} ***(1 mark)***.

c) mass = number of moles × M_r = 0.0118 × 63.5
= 0.7493 g of copper present in the brass ***(1 mark)***.
So, (0.7493 ÷ 1) × 100 = 74.93%. The brass is **74.9%** copper (to 3 s.f.) ***(1 mark)***.

Section 6 — Transition Elements

1. Transition Elements

Page 415 — Application Questions

Q1 a) $[Ar]3d^34s^2$
b) $[Ar]3d^74s^2$
c) $[Ar]3d^54s^2$
d) $[Ar]3d^84s^2$

For these questions you don't have to write [Ar]. Writing out the whole electron configuration starting from $1s^2$ is fine too.

Q2 a) $[Ar]3d^2$
b) $[Ar]3d^7$
c) $[Ar]3d^5$
d) $[Ar]3d^8$

Don't forget, the s electrons are always removed first, then the d electrons.

e) $[Ar]3d^4$
f) $[Ar]3d^1$
g) [Ar]

Q3 Zinc has the electron configuration $1s^22s^22p^63s^23p^63d^{10}4s^2$. It can only form Zn^{2+} ions which have an electron configuration of $1s^22s^22p^63s^23p^63d^{10}$. This ion has a full d-sub-shell, so zinc cannot form a stable ion with a partially filled d-sub-shell and it therefore can't be a transition metal.

Page 415 — Fact Recall Questions

Q1 In the d-block.

Q2 A transition element is a d-block element that can form one or more stable ions with an incomplete d-sub-shell.

Q3 10

Q4 Electrons fill up the lowest energy sub-shells first and electrons fill orbitals singly before they start sharing.

Q5 a) Chromium prefers to have one electron in each orbital of the 3d sub-shell and just one in the 4s sub-shell because this gives it more stability.
b) Copper prefers to have a full 3d sub-shell and one electron in the 4s sub-shell because it's more stable that way.

2. Transition Element Properties

Page 417 — Fact Recall Questions

Q1 Any two from: e.g. they can form complex ions / they form coloured ions / they make good catalysts.

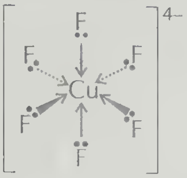
Q2 A — 3 B — 4 C — 2 D — 1

Q3 Iron

3. Complex Ions

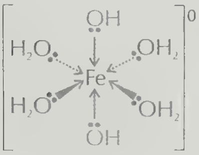
Page 420 — Application Questions

Q1 a) Octahedral:



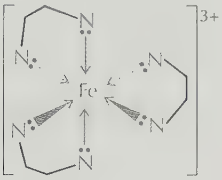
When you're drawing the shapes of ions and molecules make sure you include the dashed arrows and the wedged arrows to show that it's 3D.

b) Octahedral:



You could also draw this structure with the two $^-$OH ligands next to each other. See page 422 for more on this.

c) Octahedral:

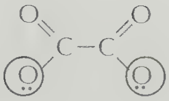


Q2 a) 6

b) 6

c) 6

Q3 a)

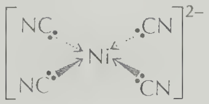


b) $[Cr(C_2O_4)_3]^{3-}$

Oxygen atoms are small so six of them will fit around a central metal ion and form coordinate bonds with it. This means that three molecules of $C_2O_4^{2-}$ will each form two coordinate bonds with the ion.

Q4 a) Square planar

b)



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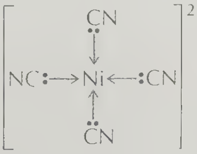


Page 420 — Fact Recall Questions

Q1 a) An atom, ion or molecule that donates a pair of electrons to a central metal ion.

b) A covalent bond where both of the electrons in the shared pair come from the same atom, ion or molecule.

c) A metal ion surrounded by coordinately bonded ligands.

Q2 A ligand that can donate two lone pairs of electrons to a central metal ion to form two coordinate bonds.

Q3 E.g. $[Fe(H_2O)_6]^{2+}$ / $[Co(NH_3)_6]^{2+}$ / $[Cu(NH_3)_4(H_2O)_2]^{2+}$.

4. Isomerism in Complex Ions

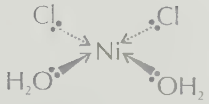
Page 422 — Application Questions

Q1 a) *cis-trans* isomerism

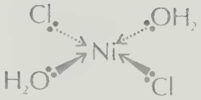
b) optical isomerism

c) *cis-trans* isomerism

Q2 E.g. *cis:*



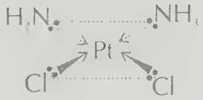
trans:



Page 422 — Fact Recall Questions

Q1 optical isomerism and *cis-trans* isomerism

Q2 a)



b) Cisplatin can bind to the DNA molecules in cancer cells and prevent them from dividing.

5. Ligand Substitution

Page 425 — Application Questions

Q1 a) octahedral

b) tetrahedral

Q2 $[Mn(H_2O)_6]^{2+}_{(aq)} + 4Cl^-_{(aq)} \rightleftharpoons [MnCl_4]^{2-}_{(aq)} + 6H_2O_{(l)}$

Q3 a) $[Cu(H_2O)_6]^{2+}_{(aq)} + 4OH^-_{(aq)}$

$\rightarrow [Cu(OH)_4(H_2O)_2]^{2-}_{(aq)} + 4H_2O_{(l)}$

b) (elongated) octahedral

Page 425 — Fact Recall Questions

Q1 a) There will be no change in coordination number or shape but the colour may change.

b) There will be a change in coordination number and shape and the colour may change.

Q2 a) It helps transport oxygen around the body.

b) Four come from nitrogen atoms in the porphyrin ring, one comes from a nitrogen atom in a globin protein and one comes from either water or oxygen.

Q3 a) In the lungs, the concentration of oxygen is high. So water ligands that were bound to the haemoglobin are substituted for oxygen ligands, forming oxyhaemoglobin.

b) At sites where oxygen is needed the concentration of oxygen is low. So oxygen ligands that were bound to haemoglobin are substituted for water ligands, forming deoxyhaemoglobin.

Q4 Carbon monoxide is a very strong ligand for haemoglobin. When it is inhaled, it binds to the central Fe^{2+} ion and prevents it from binding to oxygen. As a result, oxygen can no longer be transported around the body.

6. Precipitation Reactions

Page 427 — Application Questions

Q1 E.g. the scientist could add aqueous sodium hydroxide / ammonia to the solution. If a dark green precipitate forms iron(II) ions are present. If an orange-brown precipitate forms iron(III) ions are present.

Q2 $[Co(H_2O)_6]^{2+}{}_{(aq)} + 2NH_{3(aq)} \rightarrow Co(OH)_2(H_2O)_{4(s)} + 2NH_4{}^+{}_{(aq)}$

Page 427 — Fact Recall Questions

Q1 $[Cu(H_2O)_6]^{2+}{}_{(aq)} + 2OH^-{}_{(aq)} \rightarrow Cu(OH)_2(H_2O)_{4(s)} + 2H_2O_{(l)}$
OR $Cu^{2+}{}_{(aq)} + 2OH^-{}_{(aq)} \rightarrow Cu(OH)_{2(s)}$

Q2 An orange-brown precipitate would form in the yellow solution.

7. Transition Metals and Redox

Page 429 — Fact Recall Questions

Q1 E.g. acidified potassium manganate(VII) / $KMnO_4$

Q2 a) +3 to +6
  b) dark green to yellow
  c) dichromate(VI), $Cr_2O_7{}^{2-}$
  d) yellow to orange

Q3 Disproportionation means something is oxidised and reduced at the same time. E.g. two Cu^+ ions can disproportionate to produce Cu and Cu^{2+}.

8. Tests for Ions

Page 431 — Application Questions

Q1 Cu^{2+} and $CO_3{}^{2-}$.

$Cu^{2+}{}_{(aq)}$ ions produce a pale blue precipitate when $NaOH_{(aq)}$ is added. $CO_3{}^{2-}$ ions produce carbon dioxide when dilute hydrochloric acid is added, which turns limewater cloudy.

Q2 Both students could be correct but neither has enough evidence to be sure of their conclusion — both sulfate and carbonate ions could produce a white precipitate when barium nitrate solution is added.

Page 431 — Fact Recall Questions

Q1 a) Mn^{2+} — pale brown
  b) Fe^{2+} — pale green
  c) Cr^{3+} — dark green

Q2 a) E.g. nitric acid or hydrochloric acid.
  b) Nitric acid.

Q3 Blue.

Exam-style Questions — pages 433-435

1 C **(1 mark)**.

The electron configuration of manganese is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^2$.

2 A **(1 mark)**.

When chloride ions are added to $[Cu(H_2O)_6]^{2+}{}_{(aq)}$, $[CuCl_4]^{2-}$ is formed, which is yellow and tetrahedral.

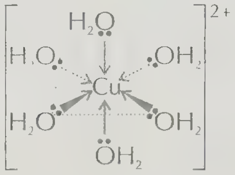
3 D **(1 mark)**.

Test 1 confirms that $Cr^{3+}{}_{(aq)}$ ions are present. Test 2 confirms that carbonate ions are not present. Test 3 confirms that chloride ions are present.

4 a) (i) pale blue ***(1 mark)***
  (ii) Cu: $1s^22s^22p^63s^23p^63d^{10}4s^1$ ***(1 mark)***
  Cu^{2+}: $1s^22s^22p^63s^23p^63d^9$ ***(1 mark)***
  (iii) Cu^{2+} has the characteristic chemical properties of transition element ions because it has a partially filled d-sub-shell ***(1 mark)***.

b) (i) A ligand is a species that donates an electron pair to form a coordinate bond with a central metal ion ***(1 mark)***.

  (ii)



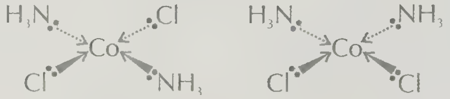
(1 mark)

Don't forget to include the charge on the complex ion when you're drawing its structure.

The shape of $[Cu(H_2O)_6]^{2+}$ is octahedral ***(1 mark)***.

  (iii) 6 ***(1 mark)***

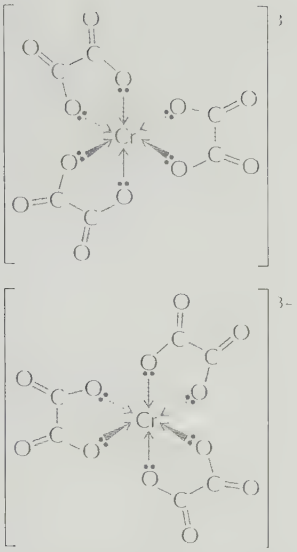
5 a) (i) square planar ***(1 mark)***
  (ii) *cis-trans* isomerism ***(1 mark)***
  (iii)



(1 mark for each correctly drawn isomer)

b) (i) optical isomerism ***(1 mark)***
  (ii) The oxygen atoms have lone pairs of electrons ***(1 mark)*** which they can donate to the chromium(III) ion to form coordinate bonds ***(1 mark)***.

(iii)



(1 mark for each correctly drawn isomer. The structures must be shown as 3D, i.e. with wedged and dotted bonds)

These are fiendishly difficult isomers to draw so don't worry if you've messed up your first few attempts. Make sure you get lots of practice drawing them before the exam and you'll be fine.

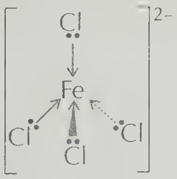
6 a) A transition element is an element that can form one or more stable ions with a partially filled d-sub-shell ***(1 mark)***.

b) (i) $[Fe(H_2O)_6]^{2+}_{(aq)} + 2OH^-_{(aq)} \rightarrow Fe(OH)_2(H_2O)_{4(s)}$
OR $Fe^{2+}_{(aq)} + 2OH^-_{(aq)} \rightarrow Fe(OH)_{2\,(s)}$ ***(1 mark)***

(ii) dark green ***(1 mark)***

c) (i) $[Fe(H_2O)_6]^{2+}_{(aq)} + 4Cl_{(aq)} \rightarrow [FeCl_4]^{2-}_{(aq)} + 6H_2O_{(l)}$
(1 mark for correct products, 1 mark for correctly balanced equation)

(ii)



(1 mark)

You need to draw the structure in 3D, with wedged and dashed bonds to get the mark here.

(iii) $[Fe(H_2O)_6]^{2+}_{(aq)} + 6CN^-_{(aq)} \rightarrow [Fe(CN)_6]^{4-}_{(aq)} + 6H_2O_{(l)}$
(1 mark)

(iv) The coordination number doesn't change because there are 6 ligands bonded to the Fe^{2+} before the reaction and 6 ligands bonded afterwards ***(1 mark)***. The shape of the complex ion doesn't change because the CN^- and H_2O ligands are similar sizes ***(1 mark)***. The colour of the complex ion may change as there has been a change in the type of ligand bonded to the Fe^{2+} ***(1 mark)***.

7 a) (i) By adding excess aqueous sodium hydroxide ***(1 mark)***.

(ii) $[Cr(H_2O)_6]^{3+} + 6OH^- \rightarrow [Cr(OH)_6]^{3-} + 6H_2O$
OR $Cr^{3+}_{(aq)} + 6OH^- \rightarrow [Cr(OH)_6]^{3-} + 6H_2O$ ***(1 mark)***

b) (i) $3H_2O_2 + 2Cr(OH)_6^{3-} \rightarrow 2OH^- + 2CrO_4^{2-} + 8H_2O$
(1 mark)

(ii) 6 ***(1 mark)***

(iii) dark green → yellow ***(1 mark)***

(iv) Add dilute sulfuric acid ***(1 mark)***.

Module 6

Section 1 — Aromatic Compounds and Carbonyls

1. Benzene

Page 439 — Application Questions

Q1 a) 1,2-dinitrobenzene
b) 4-methylphenol
c) 2,4,6-trichlorophenylamine

Q2 a) Kekulé proposed that the structure of benzene was a ring of six carbons joined by alternating double and single bonds. He later adapted his model to say that the benzene molecule was constantly flipping between two isomers.

b) The $\Delta H^\circ_{hydrogenation}$ for cyclohexene is –120 kJ mol^{-1}. So if benzene had three double bonds you would expect it to have a $\Delta H^\circ_{hydrogenation}$ of –360 kJ mol^{-1}. But, $\Delta H^\circ_{hydrogenation}$ for benzene is only –208 kJ mol^{-1}. This is far less exothermic than expected, so benzene must be more stable than the proposed Kekulé structure and the Kekulé model cannot be correct.

Page 439 — Fact Recall Questions

Q1 According to the delocalised model, the p-orbitals of all six carbon atoms overlap to create a π-system. This is made up of two ring-shaped clouds of electrons — one above and one below the plane of the six carbon atoms. All the bonds in the ring are the same and so are the same length.

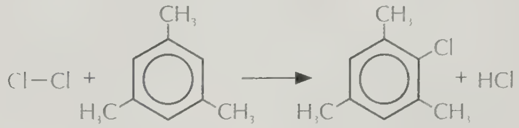
Q2 If the Kekulé model were correct, half of the bonds in benzene would be the length of C=C double bonds (134 pm) and the other half would be the length of C–C single bonds (154 pm). But X-ray diffraction studies have shown that all the bonds in benzene are the same length (140 pm — between that of single and double bonds). So this is evidence for the delocalised model.

Q3 Compounds that contain a benzene ring.

2. Reactions of Benzene

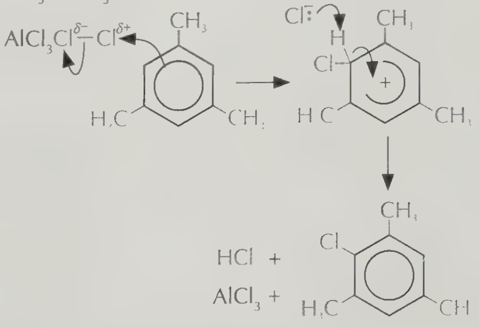
Page 443 — Application Questions

Q1 a)



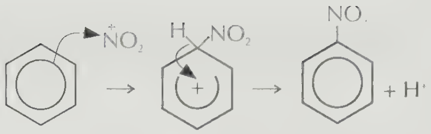
b) E.g. $AlCl_3$ / $FeCl_3$ / Fe.

c) E.g.



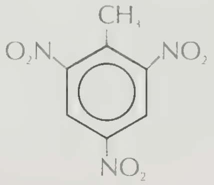
You could use another halogen carrier here (like Fe or $FeCl_3$) instead of $AlCl_3$.

Q2 a)



b) An H_2SO_4 catalyst and a temperature below 55 °C.

Q3 a)



b) The scientist needs to carry out the reaction at a temperature above 55 °C. Below this temperature he will only achieve mononitration.

Page 443 — Fact Recall Questions

Q1 In alkenes, the C=C bond is a localised area of high electron density. It attracts an electrophile, which adds to the C=C double bond, forming a stable alkane. The delocalised electrons in benzene make the benzene ring very stable, and spread out the negative charge. So benzene is very unwilling to undergo addition reactions which would destroy the stable ring.

Q2 Aromatic compounds contain a benzene ring, which is a region of high electron density. Electrophiles are electron deficient so are attracted to the regions of high electron density found in aromatic compounds.

Q3 a) Any two from, e.g. $AlCl_3$ / Fe / $FeCl_3$.

b) Br_2 isn't a strong enough electrophile to react with the benzene ring on its own.

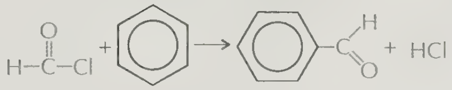
A halogen carrier will accept a lone pair of electrons from one of the bromine atoms, forming a polarised molecule, which is a much stronger electrophile than the original. This species is strong enough to react with the benzene ring.

Q4 $HNO_3 + H_2SO_4 \rightarrow HSO_4^- + NO_2^+ + H_2O$

3. Friedel-Crafts

Page 445 — Application Question

Q1 a)

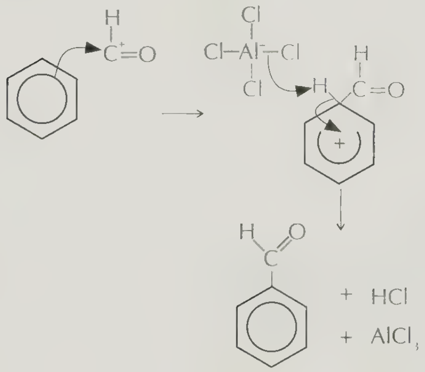


b) $AlCl_3$

c) Electrophilic substitution.

$CHOCl + AlCl_3 \rightarrow CHO^+ + AlCl_4^-$

You could draw the mechanism out with arrows or just show the equation (like above) for the first part of the mechanism.



Page 445 — Fact Recall Questions

Q1 Friedel-Crafts reactions are important to synthesis because they allow the formation of C-C bonds to an aromatic ring to happen.

Q2 $AlCl_3$ acts as a halogen carrier. It catalyses the reaction by accepting a lone pair from the acyl chloride. This increases the polarisation of the acyl chloride, and makes it a stronger electrophile so it can react with the benzene ring.

4. Substituted Benzene Rings

Page 449 — Application Questions

Q1 a) 4-bromophenol

b) 3-methyl-5-nitrophenol

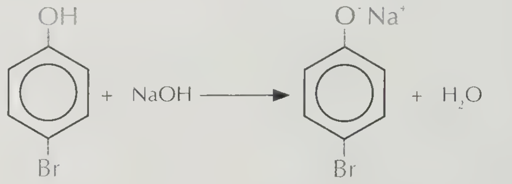
This isn't called 3-nitro-5-methylphenol because methyl comes before nitro alphabetically.

c) 3,5-dimethylphenol

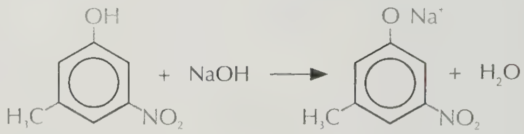
d) 4-chloro-3,5-dimethylphenol

This isn't called 3,5-dimethyl-4-chlorophenol because chloro comes before methyl alphabetically.

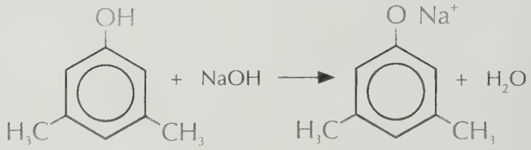
Q2 a)



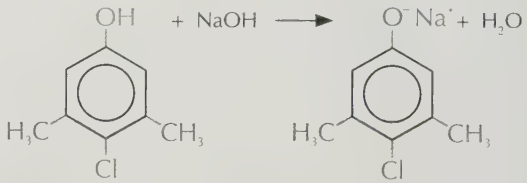
b)



c)



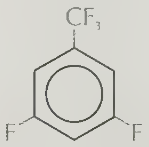
d)



Q3 Nothing would happen.

Sodium carbonate isn't a strong enough base to react with 2-methylphenol.

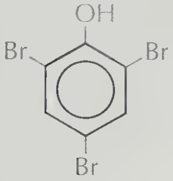
Q4



Page 449 — Fact Recall Questions

Q1 In benzene the p-orbital electrons are delocalised. This makes the benzene ring very stable so it is unwilling to undergo addition reactions with halogens. In phenol, one of the lone pairs of electrons in a p-orbital of the oxygen atom overlaps with the delocalised ring of electrons and is partially delocalised into the ring. This increases the electron density of the ring. This higher electron density means that phenol can polarise Br_2 and cause a reaction. (Benzene can't polarise Br_2 so no reaction occurs).

Q2



Q3 a) E.g. $-NO_2$

b) E.g. $-OH$, $-NH_2$

5. Aldehydes and Ketones

Page 451 — Application Questions

Q1 a) butan-2-one / butanone

You don't really need to say which carbon the functional group is on here, because it has to be carbon-2 — but in exams it's best to use the full systematic name (butan-2-one) to make sure you get the marks.

b) 2-ethyl-3-methylbutanal

Q2 2-ethyl-3-methylbutanal can be oxidised to 2-ethyl-3-methylbutanoic acid.

Q3 **C** and **D**

Q4 $CH_3CHO + [O] \rightarrow CH_3COOH$

Page 451 — Fact Recall Questions

Q1 Aldehydes have the carbonyl group at the end of the carbon chain, ketones have the carbonyl group in the middle of the carbon chain.

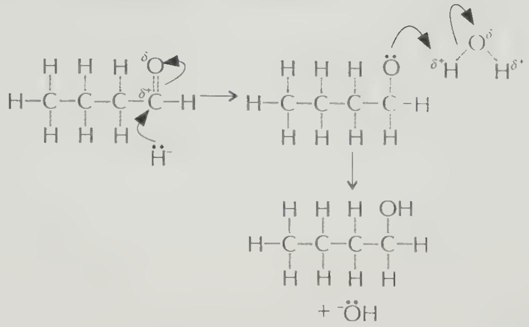
Q2 $Cr_2O_7^{2-}$

Q3 A carboxylic acid.

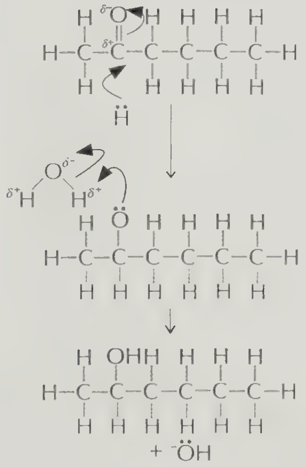
6. Reducing Carbonyls

Page 453 — Application Questions

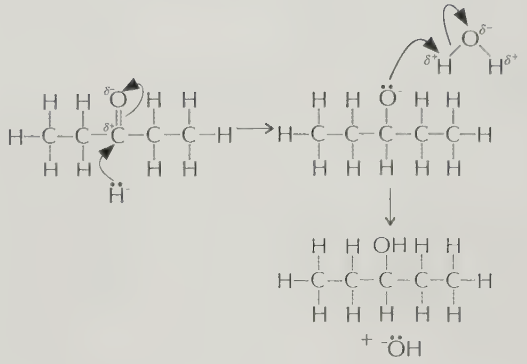
Q1 a)



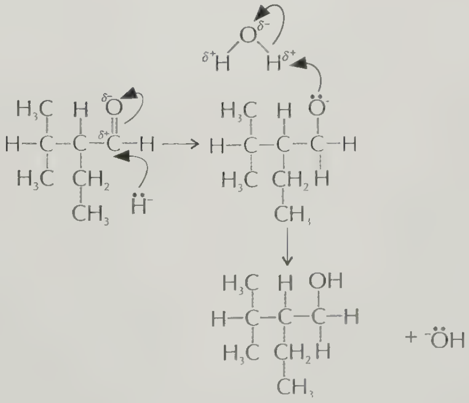
b)



c)



d)



Q2 $CH_3COCH_2CH_2CH_3 + 2[H] \rightarrow CH_3CHOHCH_2CH_2CH_3$

Q3 $CHOCH(CH_3)CH_2CH_2CH_2CH_3 + 2[H] \rightarrow$ $CH_2OHCH(CH_3)CH_2CH_2CH_2CH_3$

Q4 $CH_3COCH_2COCH_3 + 4[H] \rightarrow CH_3CHOHCH_2CHOHCH_3$

This molecule started off with two ketone groups — so when it's reduced it will end up with two alcohol groups.

Q5 $CH_3COCH(CH_3)CHO$

This is tricky — it's all about working out that molecule X must have both a ketone group and an aldehyde group if it's going to produce the molecule given in the question.

Page 453 — Fact Recall Questions

Q1 E.g. $NaBH_4$

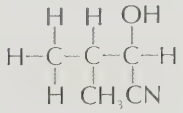
Q2 a ketone

Q3 nucleophilic addition

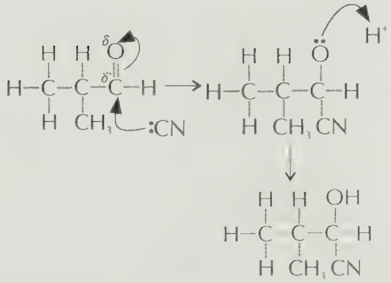
7. Reactions with Carbonyls

Page 456 — Application Questions

Q1 a)



b)



Q2 a) (i) orange precipitate formed

(ii) nothing happens

b) (i) silver mirror formed

(ii) nothing happens

Page 456 — Fact Recall Questions

Q1 carbonyl groups in aldehydes and ketones

Q2 When reacted with Brady's reagent, carbonyl compounds form derivatives of 2,4-DNPH. Each different carbonyl compound produces a crystalline derivative with a different melting point. So if you measure the melting point of the crystals and compare it against the known melting points of the derivatives, you can identify the carbonyl compound.

Q3 A solution of silver nitrate ($AgNO_3$) dissolved in aqueous ammonia.

Q4 Ag^+

8. Carboxylic Acids

Page 458 — Application Questions

Q1 a) (i) methanoic acid

(ii) 2-ethyl-4-hydroxypentanoic acid

b) $2HCOOH_{(aq)} + Mg_{(s)} \rightarrow (HCOO)_2Mg_{(aq)} + H_{2(g)}$

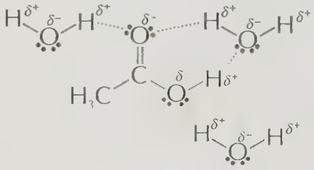
c) $2CH_3CHOHCH_2CH(C_2H_5)COOH_{(aq)} + Na_2CO_{3(s)} \rightarrow$
$2CH_3CHOHCH_2CH(C_2H_5)COONa_{(aq)} + H_2O_{(l)} + CO_{2(g)}$

Q2 $CH_3CH_2CH(CH_3)COOH_{(aq)} + NaOH_{(aq)} \rightarrow$
$CH_3CH_2CH(CH_3)COONa_{(aq)} + H_2O_{(l)}$

Page 458 — Fact Recall Questions

Q1 –COOH

Q2 Ethanoic acid is a polar molecule so it can form hydrogen bonds with water molecules. This means that it will easily dissolve in water.



Q3 A gas (hydrogen) would bubble out of the solution.

9. Acyl Chlorides

Page 460 — Application Questions

Q1 a) methanoyl chloride

b) propanoyl chloride

c) 2-methylpropanoyl chloride

Q2 a) $CHOCl + CH_3OH \rightarrow HCOOCH_3 + HCl$

b) $C_3H_5OCl + H_2O \rightarrow C_2H_5COOH + HCl$

c) $C_4H_7OCl + NH_3 \rightarrow C_3H_7CONH_2 + HCl$

Page 460 — Fact Recall Questions

Q1 $C_nH_{2n-1}OCl$

Q2 $CH_3COOH + SOCl_2 \rightarrow CH_3COCl + SO_2 + HCl$

Q3 a) A carboxylic acid and HCl.

b) An ester and HCl.

c) A primary amide and HCl.

d) A secondary amide and HCl.

10. Esters

Page 462 — Application Question

Q1 a) (i) methyl methanoate

(ii) ethyl benzoate

b) (i) methanol and methanoic acid

(ii) ethanol and benzoic acid

Page 463 — Application Questions

Q1 $CH_3CH_2CH_2OH + CH_3CH_2CH_2CH_2COOH \overset{H^+}{\rightleftharpoons}$
$CH_3CH_2CH_2CH_2COOCH_2CH_2CH_3 + H_2O$

Q2 $HCOOCHO + CH_3CH_2CH_2CH_2OH \rightarrow$
$CH_3CH_2CH_2CH_2OOCH_3 + HCOOH$

Page 464 — Application Question

Q1 a) $CH_3CH_2COOCH_3 + H_2O \overset{H^+}{\rightarrow} CH_3CH_2COOH + CH_3OH$

b) $CH_3CH_2COOCH_3 + OH^- \rightarrow CH_3CH_2COO^- + CH_3OH$

If you'd written an equation including the sodium from the sodium hydroxide that would have been fine here too ($CH_3CH_2COOCH_3 + NaOH \rightarrow CH_3CH_2COONa + CH_3OH$).

Page 464 — Fact Recall Question

Q1 a) A carboxylic acid and an alcohol.

b) A carboxylate salt and an alcohol.

Exam-style Questions — pages 466-468

Q1 C ***(1 mark)***

Q2 C ***(1 mark)***

Q3 D ***(1 mark)***

Q4 A ***(1 mark)***

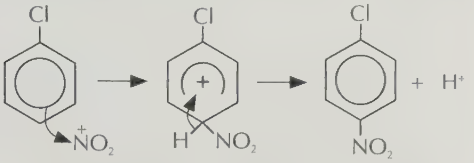
Q5 a) (i) E.g. $AlCl_3$ / $FeCl_3$ / Fe ***(1 mark)***.

You could write down any correct halogen carrier here and get the mark.

(ii) The Cl_2 isn't a strong enough electrophile to react with the benzene ring by itself ***(1 mark)***. The halogen carrier (Catalyst X) pulls electrons away from the chlorine and forms a permanent dipole ***(1 mark)***. This makes the chlorine a much stronger electrophile and gives it a strong enough charge to react with the benzene ring ***(1 mark)***.

b) (i) $HNO_3 + H_2SO_4 \rightarrow HSO_4^- + NO_2^+ + H_2O$ ***(1 mark)***

(ii)



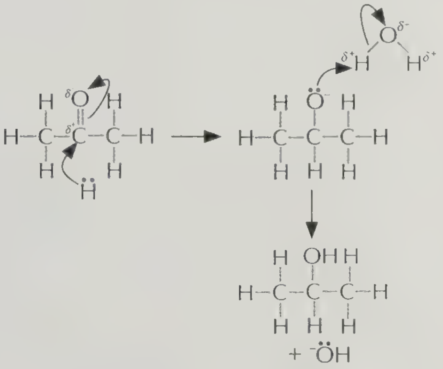
(1 mark for each correct curly arrow, 1 mark for correct intermediate, 1 mark for correct products)

(iii) 1-chloro-4-nitrobenzene ***(1 mark)***

Q6 a) molecule X — propanal ***(1 mark)***
molecule Y — propanoic acid ***(1 mark)***
molecule Z — propanone ***(1 mark)***

b) (i) E.g. $NaBH_4$ / sodium tetrahydridoborate(III) / sodium borohydride ***(1 mark)***.

(ii)



(1 mark for each correct curly arrow)

(iii) $CH_3COCH_3 + 2[H] \rightarrow CH_3CHOHCH_3$
(1 mark for correct products, 1 mark for correctly balanced equation)

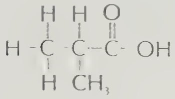
c) (i) Molecule Y is polar because electrons are drawn from the carbon to the more electronegative oxygen atom ***(1 mark)***. This means that molecule Y can form hydrogen bonds with water molecules and so will be soluble ***(1 mark)***.

(ii) $2CH_3CH_2COOH_{(aq)} + Na_2CO_{3(s)} \rightarrow$
$2CH_3CH_2COONa_{(aq)} + H_2O_{(l)} + CO_{2(g)}$
(1 mark for correct products, 1 mark for correctly balanced equation)

d) E.g. acidified potassium dichromate(VI)/$K_2Cr_2O_7$ / H_2SO_4 ***(1 mark)***.

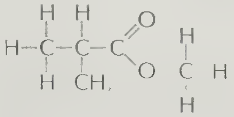
e) Molecule X (an aldehyde) will form a silver mirror with Tollens' reagent and an orange precipitate with Brady's reagent ***(1 mark)***. Molecule Y (a carboxylic acid) will not react with either reagent ***(1 mark)***. Molecule Z (a ketone) will form an orange precipitate with Brady's reagent but will not react with Tollens' reagent ***(1 mark)***.

7 a)



$H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{CH_3}{C}}-\overset{O}{\overset{\|}{C}}-OH$ ***(1 mark)***

b) (i)

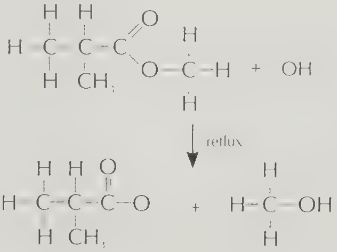


(1 mark)

(ii) methyl 2-methylpropanoate ***(1 mark)***

(iii) Any strong acid (e.g. $HCl/H_2SO_4/H_3PO_4$) ***(1 mark)***.

(iv)



(1 mark for correct equation, 1 mark for correct structure of products).

Section 2 — Nitrogen Compounds and Polymers

1. Amines and Amides

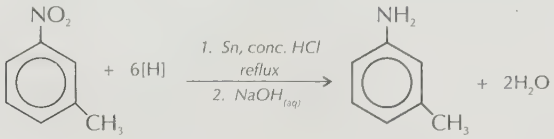
Page 472 — Application Questions

Q1 a) ethylamine
  b) dipropylamine
  c) ethyldimethylamine

Q2 $N(CH_3)_3 + HCl \rightarrow HN(CH_3)_3^+Cl^-$

Q3 $CH_3Cl + 2NH_3 \rightarrow CH_3NH_2 + NH_4^+Cl^-$

Q4



Page 472 — Fact Recall Questions

Q1 A tertiary amine is an organic molecule that consists of a nitrogen atom with three organic groups attached.

Q2 E.g. amines can act as proton acceptors by forming a dative bond with an H^+ ion. / Amines can donate their lone pair of electrons to an H^+ ion forming a dative covalent bond.

Q3 a) Heat the haloalkane with an excess of ethanolic ammonia.
  b) More than one hydrogen on the nitrogen atom from ammonia can be substituted, so a mixture of primary, secondary and tertiary amines and quaternary ammonium ions is produced.

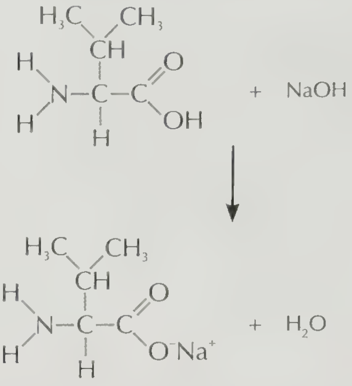
Q4 Take an aromatic nitro compound (e.g. nitrobenzene). Heat the nitro compound with tin metal and concentrated HCl under reflux to form a salt. Mix the salt with an alkali (e.g. NaOH) to produce an aromatic amine.

Q5 $-CONH_2$

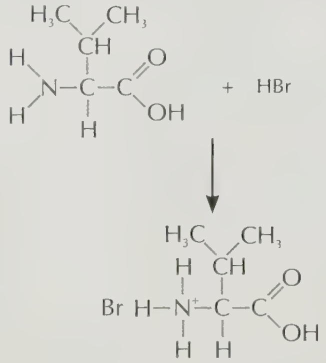
2. Amino Acids

Page 474 — Application Question

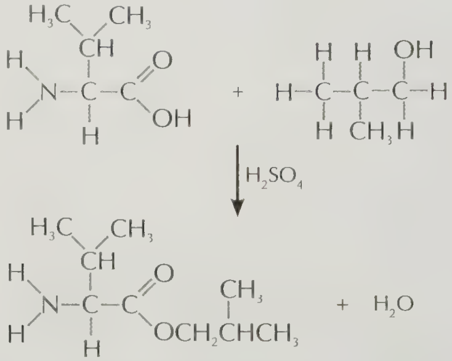
Q1 a)



b)



c)

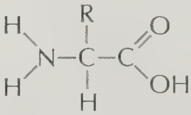


Page 474 — Fact Recall Questions

Q1 $RCH(NH_2)COOH$

Q2 Carboxyl groups (COOH) and amine groups (NH_2).

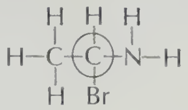
Q3



3. Chirality

Page 478 — Application Questions

Q1 a)



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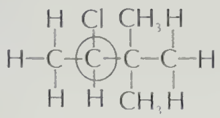

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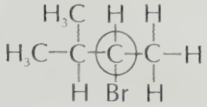
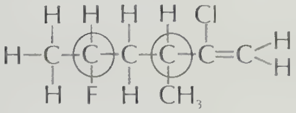
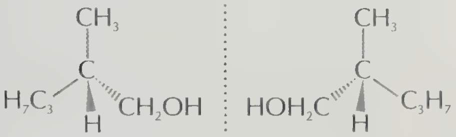


d)



Q2 a)



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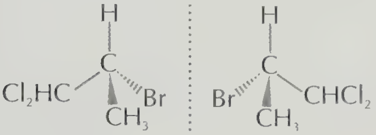

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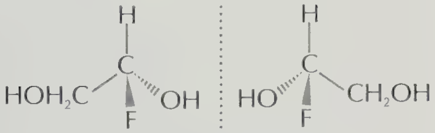
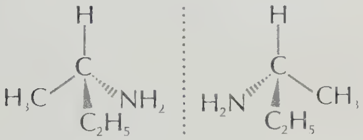
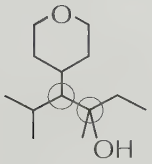


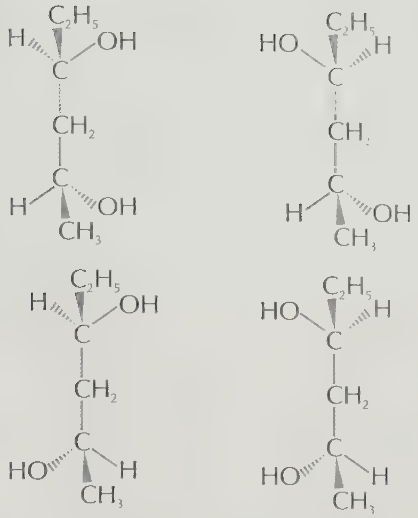
d)



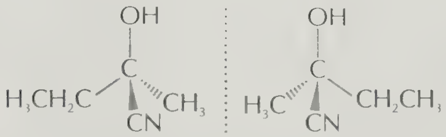
Q3



Q4



Q5



Page 478 — Fact Recall Questions

Q1 A molecule that has the same structural formula as another molecule but its atoms are arranged differently in space.

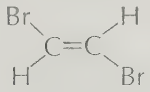
Q2 Optical isomerism is a type of stereoisomerism. In optical isomers four groups are arranged in two different ways around a central carbon atom so that two different molecules are made — these molecules are non-superimposable mirror images of each other and are called enantiomers or optical isomers.

Q3 A chiral carbon atom is one that has four different groups attached to it.

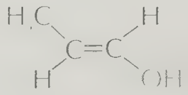
4. Addition Polymers

Page 480 — Application Questions

Q1 a)



b)



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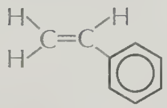
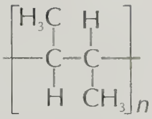
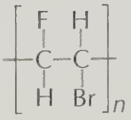


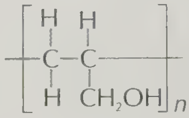
Q2 a)



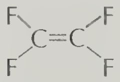
b)



c)



Q3



Page 480 — Fact Recall Questions

Q1 alkenes or substituted alkenes

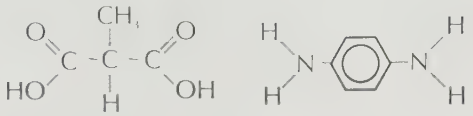
Q2 addition polymerisation

Q3 A bit of molecule that repeats over and over again.

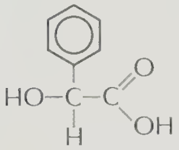
5. Condensation Polymers

Pages 486-487 — Application Questions

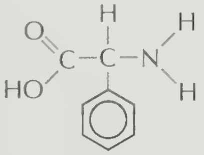
Q1 a) polyamide



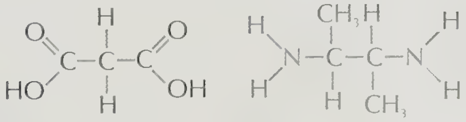
b) polyester



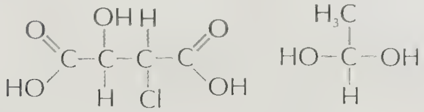
c) polyamide



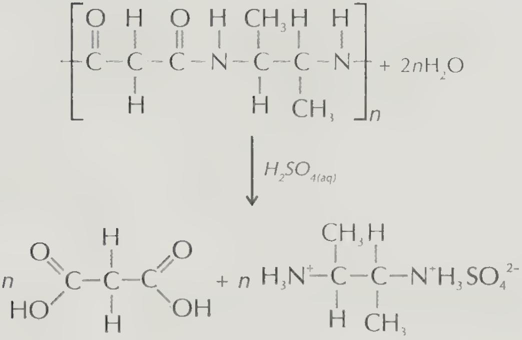
d) polyamide



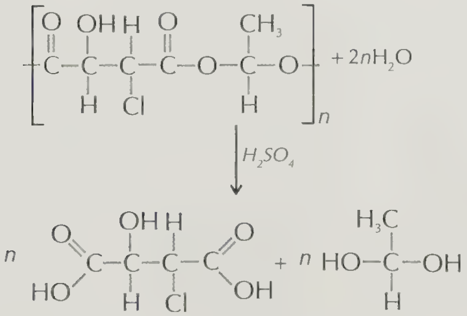
e) polyester



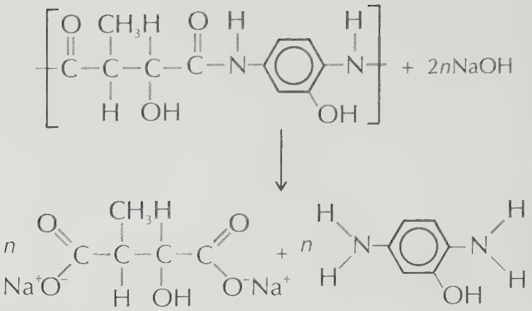
Q2 a)



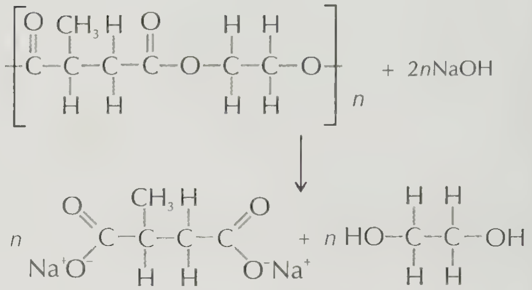
b)



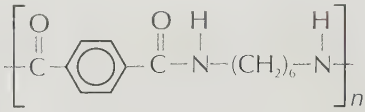
Q3 a)



b)



Q4 a)



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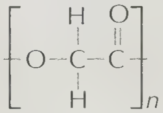
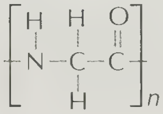
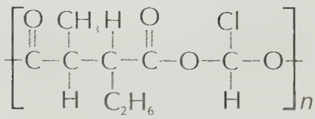


c)



d)



Page 487 — Fact Recall Questions

Q1 water

Q2 a) E.g. dicarboxylic acids and diamines.
b) E.g. dicarboxylic acids and diols.

Q3 a) amide links
b) ester links

Q4 Hydrolysis with just water is slow so an acid or an alkali is added to speed up the reaction.

Q5 E.g. a diol and a dicarboxylic acid salt.

Exam-style Questions — Pages 489-491

1 D ***(1 mark)***

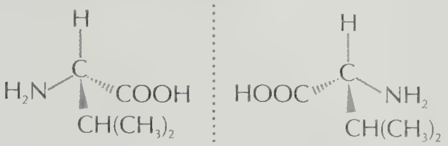
2 C ***(1 mark)***

3 B ***(1 mark)***

4 a) (i) A and C are α-amino acids ***(1 mark)***, because they have their carboxyl group and amino group attached to the same carbon ***(1 mark)***.

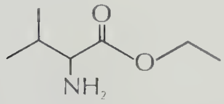
(ii) $RCH(NH_2)COOH$ ***(1 mark)***

b) (i)



(1 mark for each correctly drawn isomer)

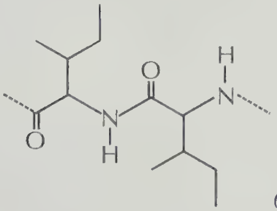
(ii)



(1 mark)

c) (i) condensation polymerisation ***(1 mark)***

(ii)



(1 mark)

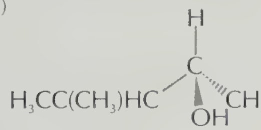
The dotted lines show that the section is part of a longer polymer. You could also have drawn a displayed formula here. As long as you show the structure correctly, any type of drawing will do.

(iii) E.g. water and an alkali catalyst ***(1 mark)***.

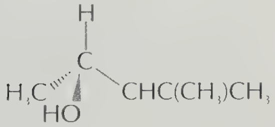
5 a) (i) Stereoisomers are molecules with the same structural formula, but different arrangements of atoms in space ***(1 mark)***. 2-methyl-2-penten-4-ol shows optical isomerism ***(1 mark)***.

(ii) It has a chiral centre ***(1 mark)***.

(iii)

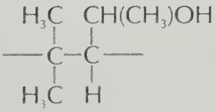


(1 mark)



(1 mark)

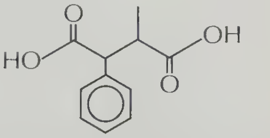
b)



(1 mark)

c) Yes because it has a chiral carbon atom ***(1 mark)***.

d) (i)



(1 mark)

It doesn't matter how you draw the molecule — whether you use a skeletal formula like this, or a displayed formula. As long as it's correct, you'll get the mark.

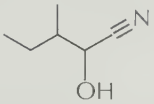
(ii) polyester ***(1 mark)***

Section 3 — Organic Synthesis and Practical Techniques

1. Making Carbon-Carbon Bonds

Page 497 — Application Questions

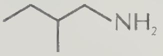
Q1 a)



b) E.g. reflux, dilute hydrochloric acid

Q2 a) E.g. reflux, ethanol and NaCN / HCN / KCN

b)



c) E.g. reflux, benzene, $AlCl_3$ (catalyst)

Page 497 — Fact Recall Questions

Q1 A nucleophilic substitution reaction.

Q2 A hydroxynitrile.

Q3 E.g Friedel-Crafts acylation and Friedel-Crafts alkylation.

2. Practical Techniques in Organic Synthesis

Page 500 — Application Questions

Q1 For recrystallisation to work, benzoic acid needs to be soluble in the hot solvent, but insoluble in the cold solvent. This means water is an appropriate choice of solvent for recrystallising benzoic acid.

Q2 Sample B is the least pure, followed by Sample C and then Sample A. Purity can be determined by how close the sample's melting point is to the standard value. The lower the melting point compared to the standard value, the less pure the sample will be. Also, the greater the range in melting point, the less pure the sample will be. Sample B has the lowest melting point compared to the standard value (138-140 °C), and the greatest range in its melting point, so it is the least pure sample. Sample A has a melting point very close to the standard value, and the range is also the smallest of the three samples, so it will be the most pure.

Page 500 — Fact Recall Questions

Q1 Reflux

Q2 To remove any liquid impurities from the solid.

Q3 E.g. Determine the melting point of the solid compared to the standard value of the pure solid.

3. Functional Groups and their Typical Reactions

Page 503 — Application Questions

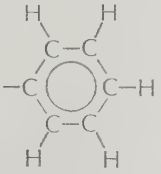
Q1 a) alkenyl/alkene, haloalkane/bromoalkane, aldehyde

b) The molecule contains an aldehyde functional group which can be oxidised to form a carboxylic acid group.

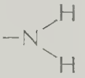
Q2 a) A b) A and C c) B and C

Page 503 — Fact Recall Questions

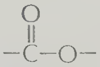
Q1 a)



b)



c)



Q2 a) nitrile

b) (primary) amide

c) aldehyde

4. Synthetic Routes

Page 506 — Application Questions

Q1 a) H_3PO_4 catalyst, steam, 300 °C, 60-70 atm
b) Br_2, U.V. light

Q2 a) E.g. step 1: NaOH/KOH, H_2O, reflux
step 2: $K_2Cr_2O_7$, H_2SO_4, heat in distillation apparatus
You have to do this reaction in distillation apparatus so that you don't form the carboxylic acid.
b) E.g. step 1: $K_2Cr_2O_7$, H_2SO_4, reflux
step 2: methanol, conc. H_2SO_4, heat under reflux
You can't reduce the butanal to butan-1-ol and then react it with methanoic acid to get the ester — you'd end up with butyl methanoate, rather than methyl butanoate.

Q3 X is nitrobenzene. Y is phenylamine.

Q4 E.g. step 1: $NaBH_4$, then water
step 2: concentrated H_2SO_4/H_3PO_4 catalyst, 170 °C
step 3: Br_2, 20 °C

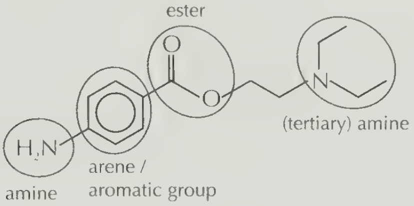
Q5 E.g. step 1: HBr, 20 °C
step 2: warm NaOH/KOH, H_2O, reflux
step 3: $K_2Cr_2O_7$, H_2SO_4, reflux

Page 506 — Fact Recall Questions

Q1 alkane, alcohol, alkene
Q2 alcohol, carboxylic acid, hydroxynitrile
Q3 acyl chloride, 20 °C

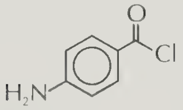
Exam-style Questions — Pages 508-509

1 B *(1 mark)*
2 B *(1 mark)*
3 A *(1 mark)*
4 a)



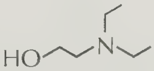
(2 marks — 1 mark for correctly circling all the functional groups, 1 mark for correct names.)

b) (i)



(1 mark)

(ii) The reagent is:

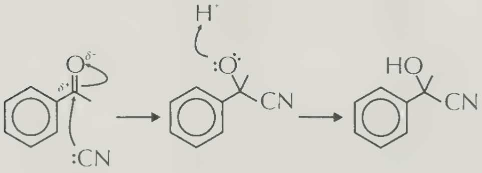


(1 mark).

The conditions are 20 °C / room temperature *(1 mark)*.

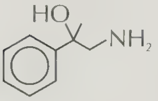
c) (i) The sample is impure *(1 mark)*.
(ii) e.g. recrystallisation *(1 mark)*

5 a) e.g. ethanoyl chloride, $AlCl_3$ (catalyst), reflux *(1 mark)*
b) (i) HCN *(1 mark)*
(ii) The reaction occurs via a nucleophilic addition mechanism *(1 mark)*:



(3 marks — 1 mark for each correct curly arrow)

c)



(1 mark)

Section 4 — Analysis

1. Tests for Organic Functional Groups

Page 513 — Application Questions

Q1 a bromoalkane

Q2 E.g. You could identify which test tube contained propanal using Tollens' reagent. Tollens' reagent is prepared by adding silver nitrate solution to a test tube and adding sodium hydroxide, so that a light brown precipitate forms. Dilute ammonia solution is then added until the precipitate dissolves. This solution is Tollens' reagent. It reacts with propanal, an aldehyde, when warmed, to produce a silver mirror. No reaction would be seen with propanone or propanoic acid. To identify which of the remaining test tubes contains propanoic acid, add 1 small spatula of solid calcium carbonate to a sample of each substance. The carboxylic acid will react with the calcium carbonate (seen as fizzing) to produce carbon dioxide gas which, when bubbled through limewater, will turn limewater cloudy. The remaining test tube will contain propanone as it does not react with calcium carbonate.

Q3 a) The acidified potassium dichromate(VI) solution would change from orange to green.
b) The limewater would turn cloudy.

Page 513 — Fact Recall Questions

Q1 bromine water
Q2 pale yellow
Q3 Add a sample of the unknown compound to a test tube and add 1 small spatula of solid sodium hydroxide/2 cm^3 of sodium hydroxide solution. If the solution fizzes and a colourless solution forms, then add another sample of the unknown compound to a separate test tube. Add 1 small spatula of solid sodium carbonate/2 cm^3 of sodium carbonate solution. If nothing happens, the unknown compound must be a weak acid, and so must be a phenol.
Q4 A bright orange precipitate would form.

2. Chromatography

Page 515 — Application Question

Q1 a) $R_f \text{ value} = \dfrac{\text{distance travelled by spot}}{\text{distance travelled by solvent}}$
Spot P: R_f value = 2.1 ÷ 8.0 = **0.26**
Spot Q: R_f value = 3.7 ÷ 8.0 = **0.46**
Spot R: R_f value = 5.9 ÷ 8.0 = **0.74**
b) Spot P contains glycine, spot Q contains tyrosine and spot R contains leucine.
c) The student could check each amino acid has been identified correctly by running a pure sample of each amino acid, alongside the mixture of amino acids, on the same TLC plate. The pure amino acids should travel the same distance up the plate/have the same R_f values as the corresponding amino acids in the mixture.

Page 515 — Fact Recall Questions

Q1 How far each part of the mixture travels up the plate depends on how strongly it's adsorbed to the surface of the plate.
A substance that's strongly adsorbed spends more time stuck to the plate and less time dissolved in the solvent, so it moves slowly and doesn't travel as far as a weakly adsorbed substance. So the mixture separates out.
Remember, adsorption is the important idea here — as long as you're talking about differences in the strength of adsorption of the different components, you're on the right track.

Q2 $R_f \text{ value} = \dfrac{\text{distance travelled by spot}}{\text{distance travelled by solvent}}$

Q3 E.g. the solid coating on the TLC plate, the solvent, the temperature.

3. Gas Chromatography

Page 519 — Application Questions

Q1 Components that are more soluble in the oil take longer to travel through the tube, so the pure product will reach the detector after the impurities.

Q2 a) peak A
b) component B
c) component C

Q3 a) Total peak area = 32 + 16 = 48 cm^2
% of mixture that is Chemical 2 = (16 ÷ 48) × 100
= **33%**

This question is all about applying your maths and chemistry knowledge to a situation you've not met before. Don't panic if you get questions like these, that you may not have practised, in the exam. Just stay calm, think about exactly what the question asks and tells you, and you should be fine.

b) 1.32 mol dm^{-3}

Page 519 — Fact Recall Questions

Q1 Some of the components in a mixture will be more soluble in the liquid than others. This means that the components will spend different amounts of time dissolved in the liquid and travelling along the tube in the gas. So they will take different amounts of time to pass through the tube and will be separated out.

Q2 The time taken from the injection of a sample to the detection of a substance.

Q3 The area under each peak tells you the relative amount of each component that's present in the mixture.

Q4 E.g. first you need to create a series of standard solutions of different concentrations of analyte. One by one, inject the standard solutions into a gas chromatography instrument and record the result. Calculate the area under the peak corresponding to each standard solution. Correct the area of the peak for each concentration, using the chromatogram of a blank solution. Plot these values on a graph of area vs concentration. Then draw a line of best fit to create an external calibration curve.

4. NMR Spectroscopy

Page 524 — Application Questions

Q1 a) 4

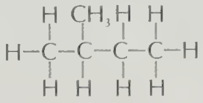
The number of peaks on the ^{13}C NMR spectrum is the same as the number of carbon environments in the molecule...

b) 3
c) 2

This one's a bit tricky. If you draw the molecule, you should see that three of the carbons are CH_3 groups joined to the central carbon atom. These carbons are all in the same environment.

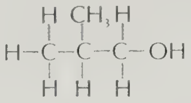
d) 4

Q2 There are four peaks on the spectrum, so the molecule must have four carbon environments. All the peaks lie between $\delta = 10$ ppm and $\delta = 40$ ppm. Since the molecule only contains carbon and hydrogen, these must all represent carbon atoms in alkyl groups. The formula of the molecule is C_5H_{12}, so it must be an isomer of pentane with four carbon environments.
The only molecule that fits this description is **2-methylbutane**:



Carbon 1 and the methyl group carbon are in the same environment. Carbons 2, 3 and 4 are all in different environments.

Q3 a) A carbon in a C–O environment.
b) There are three peaks on the spectrum, so the molecule must have three carbon environments. The peaks at $\delta = 8$ ppm and $\delta = 25$ ppm must represent carbons in alkyl groups. The peak at $\delta = 65$ ppm must represent a carbon in a C–O bond. The formula of the molecule is $C_4H_{10}O$ and it must have three carbon environments. The only molecule that fits this description is **2-methylpropan-1-ol**:



Q4 D

There are four different carbon environments so there should be four peaks. There is one C=O environment which will have a peak between $\delta = 160$ ppm and $\delta = 220$ ppm. There are two different C=C environments which will have peaks between $\delta = 115$ ppm and $\delta = 160$ ppm. There is one C–C environment which will have a peak between $\delta = 0$ ppm and $\delta = 50$ ppm. This matches the information shown on spectrum D.

Page 524 — Fact Recall Questions

Q1 tetramethylsilane/TMS

Q2 The number of carbon environments in the molecule.

5. Proton NMR Spectroscopy

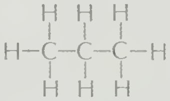
Page 527 — Application Questions

Q1 a) 2

That's one environment for the two hydrogens on carbon 1, and one environment for the three hydrogens on carbon 3.

b) 2

Q2 E.g.



This is propane. You could also have had other things like butane or 2-methylpropane, but not ethane — that's only got one hydrogen environment.

Q3 a) 2

b) 1 : 3

c) 2 in environment A and 6 in environment B.

You need to divide up the eight hydrogens between the two environments so that they end up in the ratio 1 : 3.

Q4 a) hydrogen atoms in an R–CH group

b) hydrogen atoms in an HC=C– group

You'd get the mark here for anything that showed clearly that you were talking about the right group (e.g. 'an H attached to a C=C group' or 'an H in an alkene group' would do for part b).

Q5 a) 2

b) 1 : 1

c) There will be one peak at δ = 2-3 ppm and another at δ = 3-4 ppm.

Page 527 — Fact Recall Questions

Q1 The number of hydrogen environments in the molecule.

Q2 The relative number of H atoms in each environment.

Q3 The relative areas under the peaks (and so the relative number of H atoms in each environment in the molecule).

6. More Proton NMR Spectroscopy

Page 529 — Application Questions

Q1 2

Think about the n + 1 rule — if the carbon next door has two hydrogens on it the peak will split into 2 + 1 = 3.

Q2 Environment 1: peak is a singlet / not split.
Environment 2: peak split into four / quartet.
Environment 3: peak split into two / doublet.

Page 532 — Application Questions

Q1 There are three peaks, so there must be three hydrogen environments in compound **X**.

The peak at δ = 2.5 ppm is likely to be formed by hydrogens in a –COCH– environment.

It can't be an R –NH, an HC–N or a methylbenzene environment because none of those would fit with the molecular formula. And it can't be an R–OH group because the peak isn't a singlet.

The peak at δ = 2.1 ppm is also likely to be formed by hydrogens in a –COCH– environment.

This isn't likely to be an R–OH group because the area ratio tells you that the environment contains more than one hydrogen.

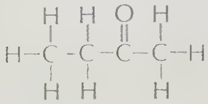
The peak at δ = 1 ppm is likely to be formed by hydrogens in an R–CH environment.

It can't be an R –NH group because that wouldn't fit with the formula, and it isn't an R–OH group because it isn't a singlet.

From the area ratios, there are two protons in the environment at δ = 2.5 ppm for every three protons in the environment at δ = 2.1 ppm and for every three protons in the environment at δ = 1 ppm. To fit this data, the groups contained in compound **X** must be $-COCH_2-$, $-COCH_3$ and $-CH_3$.

We know that the molecular formula is C_4H_8O and that the $-CH_3$ group must be next to the $-COCH_2-$ (because their peaks are split into a triplet and a quartet).

So, the molecule must be **butan-2-one**:



Q2 There are three peaks, so there must be three hydrogen environments.

The peak at δ = 1.1 ppm is likely to be formed by hydrogens in an R–CH environment.

It can't be an R–OH group or an R–NH group because you don't find either of those groups in esters.

The peak at δ = 2.3 ppm is likely to be formed by hydrogens in a –COCH– environment.

Again, it can't be any of the other groups that cause peaks at that chemical shift, because none of them appear in an ester.

The peak at δ = 3.7 ppm is likely to be formed by hydrogens in a HC–O– environment.

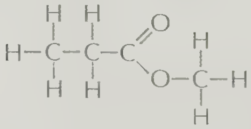
And again — an ester doesn't contain any of the other groups that could be causing a peak at this chemical shift.

From the area ratios, there are three protons in the environment at δ = 1.1 ppm for every two protons at δ = 2.3 ppm and for every three protons at δ = 3.7 ppm.

To fit this data, the groups must be $-CH_3$, $-COCH_2-$ and $-O-CH_3$.

The peak at δ = 1.1 ppm is a triplet, suggesting that it is adjacent to a carbon with two hydrogens. The peak at δ = 2.3 ppm is a quartet, suggesting that it is adjacent to a carbon with three hydrogens. So these two groups must be next door to each other, giving $CH_3-CH_2C(O)-$. The peak at δ = 3.7 ppm is a singlet, so the $-O-CH_3$ group is not adjacent to any other hydrogens. So the molecule is an ester containing the groups $CH_3-CH_2C(O)-$ and $-O-CH_3$.

It must be **methyl propanoate**:



Q3 There are two different hydrogen environments so there will be two peaks. The $-H_2CC(O)-$ environment will have a peak between δ = 2 ppm and δ = 3 ppm and the peak will be a quartet, because there are three hydrogens on the adjacent carbon. The $-CH_3$ environment will have a peak between δ = 0.5 ppm and δ = 2 ppm and the peak will be a triplet, because there are two hydrogens on the adjacent carbon.

Page 532 — Fact Recall Questions

Q1 The rule that states that, in proton NMR spectroscopy, peaks always split into the number of non-equivalent hydrogens on the neighbouring carbons, plus one.

Q2 a quartet

Q3 e.g. $CDCl_3$

Remember — the important thing here is that solvents for proton NMR can't contain any H atoms.

Q4 Run a proton NMR spectrum for the sample molecule just as normal. Then run another one with a little deuterium oxide/ D_2O, added. If an OH proton is present, it'll swap with deuterium (to become an OD group). So the peak that was caused by the OH group on the first spectrum will be absent from the second spectrum.

7. More on Spectra

Pages 536-537 — Application Questions

Q1 The mass spectrum shows that the M_r of the molecule is 58. It has a peak at m/z = 15, so it may contain a CH_3 group. It has a peak at 43, so it may contain a CH_3CO group or a $CH_3CH_2CH_2$ group.

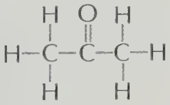
The IR spectrum has a peak at 1700 cm^{-1}, so the molecule contains a carbonyl (C=O) group. As there are no peaks between 2500 cm^{-1} and 3300 cm^{-1} it can't contain any O–H or N–H bonds. So it isn't a carboxylic acid or an amide.

The ^{13}C NMR spectrum has two peaks, so the molecule has two carbon environments. The peak at $\delta = 205$ ppm is a carbon in a ketone or aldehyde group. The peak at $\delta = 29$ ppm is a carbon in a C–C group.

The proton NMR spectrum has one singlet peak, so the molecule has one hydrogen environment and there are no hydrogen atoms on adjacent carbons. This singlet peak at $\delta = 2.3$ ppm must be caused by hydrogens in a –CHCO– environment.

All the other groups that cause peaks at this chemical shift have been ruled out by the mass spectrum and IR spectrum.

The molecule must be a ketone or aldehyde with an M_r of 58 — so it must be propanone (CH_3COCH_3) or propanal (CH_3CH_2CHO). Propanone has two carbon environments and one hydrogen environment. Propanal has three carbon environments and three hydrogen environments. So the molecule must be **propanone**:



$$\begin{array}{ccccc} & H & O & H & \\ & | & \| & | & \\ H- & C- & C- & C & -H \\ & | & & | & \\ & H & & H & \end{array}$$

It doesn't matter if you haven't answered this in exactly the same way as long as you've got most of the info down...

Q2 Mass of each element in 100 g:

C = 55.0 g H = 9.0 g O = 36.0 g

Moles of each element:

C= (55 ÷ 12) = 4.6 moles

H = (9.0 ÷ 1) = 9.0 moles

O = (36 ÷ 16) = 2.3 moles

Divide each by 2.3:

C = (4.6 ÷ 2.3) ≈ 2 H = (9.0 ÷ 2.3) ≈ 4

O = (2.3 ÷ 2.3) ≈ 1

The ratio of C : H : O is 2 : 4 : 1.

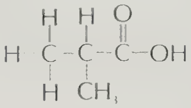
So the empirical formula is C_2H_4O and empirical mass is (2 × 12) + (4 × 1) + 16 = 44 g

88 ÷ 44 = 2, so molecular formula is 2 times the empirical formula. The molecular formula is $C_4H_8O_2$.

The IR spectrum has a strong peak at 1700 cm^{-1} and a broad peak at 3000 cm^{-1}, so it must contain a C=O bond and an O–H bond in a carboxylic acid group. Therefore, the molecule must be a carboxylic acid.

The ^{13}C NMR spectrum has three peaks, so the molecule must have three carbon environments.

There are only two carboxylic acids with the formula $C_4H_8O_2$ — butanoic acid ($CH_3CH_2CH_2COOH$) and 2-methylpropanoic acid ($(CH_3)_2CHCOOH$). Butanoic acid has four carbon environments, but 2-methylpropanoic acid has three. So the molecule must be 2-methylpropanoic acid:



$$\begin{array}{ccccc} & H & H & O & \\ & | & | & \| & \\ H- & C- & C- & C & -OH \\ & | & | & & \\ & H & CH_3 & & \end{array}$$

Exam-style Questions — pages 538-540

1 D ***(1 mark)***

Only weak acids, such as phenol, will react with sodium hydroxide but not sodium carbonate. A and B are weak bases so would not react with sodium hydroxide or sodium carbonate, and C is a strong acid so would react with sodium hydroxide and sodium carbonate.

2 B ***(1 mark)***

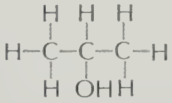
3 C ***(1 mark)***

Only aldehydes will react with Tollens' reagent to form a silver mirror. The molecule in the question is a ketone, so nothing will happen.

4 a) E.g. $CDCl_3$ ***(1 mark)***.

Any deuterated solvent would get the mark here.

b) The molecule is propan-2-ol:



$$\begin{array}{ccccc} & H & H & H & \\ & | & | & | & \\ H- & C- & C- & C & -H \\ & | & | & | & \\ & H & OH & H & \end{array}$$

(1 mark for correctly identifying the molecule)

Plus any five from: There are three peaks, so the molecule must have three hydrogen environments ***(1 mark)***. The peak at $\delta = 0.9$ ppm must be due to hydrogens in an R–CH environment ***(1 mark)***.

This peak is a doublet, so there must be one hydrogen on adjacent carbons ***(1 mark)***. The singlet peak at $\delta = 2.2$ ppm must be due to a hydrogen in the alcohol group / an R–OH environment ***(1 mark)***. The peak at $\delta = 4.0$ ppm must be due to a hydrogen in an HC–O environment ***(1 mark)***. It is a heptet, so there must be six hydrogens on adjacent carbons ***(1 mark)***.

c) The (singlet) peak at $\delta = 2.2$ ppm would be missing ***(1 mark)***.

5 a) Some components of the mixture will be more strongly adsorbed to the stationary phase than others ***(1 mark)***. So the components will spend different amounts of time adsorbed to the stationary phase and will travel different distances up the plate ***(1 mark)***.

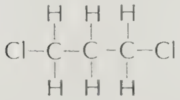
b) R_f value = $\frac{\text{distance travelled by spot}}{\text{distance travelled by solvent}}$

= 2.2 cm ÷ 9.2 cm = **0.24** ***(1 mark)***

c) The unknown carbonyl is either propanone or propanal. To identify it, the scientist could react the unknown carbonyl with Tollens' reagent ***(1 mark)***. If the compound is propanone, nothing will happen ***(1 mark)***. If the unknown carbonyl is propanal, a silver mirror will form on the walls of the test tube ***(1 mark)***.

d) An alkene ***(1 mark)***.

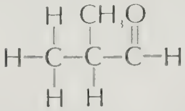
6 a) The compound has two hydrogen environments ***(1 mark)***. The peak at δ = 1.8 ppm must represent hydrogens in R–CH environments ***(1 mark)***. The peak at δ = 3.8 ppm must come from hydrogens in an HC–Cl environment ***(1 mark)***. The peak at δ = 1.8 ppm is a quintet, so there must be four hydrogens on adjacent carbons ***(1 mark)***. The peak at δ = 1.8 ppm is a triplet, so there must be two hydrogens on adjacent carbons ***(1 mark)***. The only molecule with the formula $C_3H_6Cl_2$ that would fit this pattern of environments is 1,3-dichloropropane:



$$Cl{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}Cl$$

(1 mark)

b) The molecule is methylpropanal:



$$H{-}\overset{H}{\underset{H}{C}}{-}\overset{CH_3}{\underset{H}{C}}{-}\overset{O}{\overset{\|}{C}}{-}H$$

(1 mark for correctly identifying the molecule)

Plus any four from: the molecular ion peak on the mass spectrum is at m/z = 72, so the molecular mass of the molecule must be 72 ***(1 mark)***. The mass spectrum has a peak at m/z = 15, so the molecule probably contains a CH_3 group ***(1 mark for any peak on the mass spectrum matched to a correct fragment of the molecule)***. The ^{13}C NMR spectrum has three peaks, so the molecule must have three carbon environments ***(1 mark)***. There is a peak at δ = 15 ppm and another at δ = 35 ppm, so the molecule must contain at least two carbons in C–C environments ***(1 mark)***. There is a peak at δ = 205 ppm, so the molecule must contain at least one carbon in an aldehyde or ketone C=O environment ***(1 mark)***. There are only three isomers that are aldehydes or ketones with an M_r of 72 — butanone, butanal and methylpropanal. ***(1 mark for any representation of the three possible isomers)***. Methylpropanal is the only possible isomer that has three carbon environments ***(1 mark)***.

There are usually more things to say than there are marks for this type of question, so you don't need to say all of this to get full marks. Just make sure you've made it clear to the examiner how you got to your answer.

Glossary

A

α-amino acid
An amino acid with the amino group and the carboxylic acid group attached to the same carbon.

Accurate result
A result that is close to the true answer.

Acid
A substance that releases hydrogen ions (H^+) in aqueous solution (a proton donor).

Acid dissociation constant, K_a
An equilibrium constant specific to weak acids that relates the acid concentration to the concentration of $[H^+]$ ions. $K_a = [H^+][A^-] \div [HA]$.

Acidic buffer
A buffer with a pH of less than 7 made by mixing a weak acid with a salt of its conjugate base or by adding a small amount of strong alkali to an excess of weak acid.

Activation energy
The minimum amount of kinetic energy that particles need to have in order to react when they collide.

Acyl chloride
An organic compound with the functional group –COCl.

Acylation
When an acyl group (–COR) is added to a molecule.

Addition polymer
A type of polymer formed by joining lots of small alkenes (monomers) together.

Addition reaction
A reaction where two molecules join together to form a single product.

Adsorption
The attraction between a substance and the surface of a solid.

Alcohol
A substance with the general formula $C_nH_{2n+1}OH$.

Aldehyde
A substance with the general formula $C_nH_{2n}O$ which has a hydrogen and one alkyl group attached to the carbonyl carbon atom.

Alicyclic compound
An organic compound that contains carbon and hydrogen joined together in a non-aromatic ring.

Aliphatic compound
An organic compound that contains carbon and hydrogen joined together in straight chains, branched chains or non-aromatic rings.

Alkali
A base that is soluble in water and releases hydroxide ions (OH^-) in aqueous solution.

Alkaline earth metal
An element in Group 2 of the periodic table.

Alkane
A hydrocarbon with the general formula C_nH_{2n+2}.

Alkene
A hydrocarbon with the general formula C_nH_{2n} and containing at least one carbon-carbon double bond.

Alkyl group
A hydrocarbon fragment with the general formula C_nH_{2n+1}.

Alkylation
When an alkyl group is added to a molecule.

Amide
A carboxylic acid derivative containing the functional group -$CONH_2$.

Amide link
The -CONH- group which is found between monomers in a polyamide.

Amine
A molecule where one or more of the hydrogen atoms in ammonia have been replaced with an alkyl group.

Amino acid
A molecule with an amino group (NH_2) and a carboxyl group (COOH)

Anhydrous salt
A salt that doesn't contain any water of crystallisation.

Anomalous result
A result that doesn't fit in with the pattern of the other results in a set of data.

Antacid
A substance which neutralises stomach acid.

Aromatic compound
An organic compound that contains a benzene ring.

Arrhenius equation
An equation linking the rate constant of a reaction to the activation energy and temperature.

Arrhenius plot
A graph where 1/temperature is plotted against ln *k*, where *k* is the rate constant.

Atom
A neutral particle made up of protons and neutrons in a central nucleus, and electrons orbiting the nucleus.

Atom economy
The proportion of reactant atoms that become part of the desired product, expressed as a percentage.

Atomic (proton) number
The number of protons in the nucleus of an atom.

Atomic radius
The distance between the nucleus of an atom and its outermost electrons.

Average bond enthalpy
The energy needed to break one mole of a bond in the gas phase, averaged over the different compounds that the bond is found in.

Avogadro constant
6.02×10^{23} — the number of particles in 1 mole of a substance.

B

Balanced equation
An equation that has the same number of each type of atom and the same overall charge on each side.

Base
A substance that removes hydrogen ions (H^+) from an aqueous solution (a proton acceptor).

Benzene
An organic compound with the formula C_6H_6. Its six carbon atoms are joined together in a ring. The ring is planar (flat) and the hydrogens all stick out in the same plane.

Bidentate ligand
A ligand that can form two coordinate bonds.

Biodegradable
A substance that naturally decomposes because organisms can digest it.

Bohr model
A model for the structure of an atom proposed by Niels Bohr.
He suggested that electrons only exist in fixed orbitals (shells) and not anywhere else.

Boltzmann distribution
A theoretical model that describes the distribution of kinetic energies of molecules in a gas.

Bond enthalpy
The energy required to break a bond between two atoms. Usually given as an 'average bond enthalpy' (an average value for the particular bond over the range of compounds it is found in).

Bond fission
The process of breaking a covalent bond.

Born-Haber cycle
An enthalpy cycle that allows you to calculate the lattice enthalpy for a system.

Brady's reagent
2,4-dinitrophenylhydrazine (2,4-DNPH) dissolved in methanol and concentrated sulfuric acid.
Used to test for carbonyl compounds (aldehydes and ketones).

Brønsted-Lowry acid
A proton donor.

Brønsted-Lowry base
A proton acceptor.

Buffer
A solution that minimises changes in pH when small amounts of acid or alkali are added.

C

Carbocation
An organic ion containing a positively charged carbon atom.

Carbon skeleton
The arrangement of all the carbon atoms in an organic compound.

Carbonyl compound
An organic compound that contains a carbon-oxygen double bond.

Carboxylic acid
A substance which has a COOH group attached to the end of a carbon chain.

Catalyst
A substance that increases the rate of a reaction by providing an alternative reaction pathway with a lower activation energy. The catalyst is chemically unchanged at the end of the reaction.

Catalytic converter
A device fitted to car exhausts to remove pollutant gases such as carbon monoxide, nitrogen monoxide and unburnt hydrocarbons.

Categoric data
Data that can be sorted into categories.

Causal link
The relationship between two variables where a change in one variable causes a change in the other.

Cell potential (E_{cell})
The voltage between two half-cells in an electrochemical cell.

Chain isomer
A molecule that contains the same atoms as another molecule but has a different arrangement of the carbon skeleton.

Charge density
The amount of charge in relation to the size of an ion.

Chemical shift
Nuclei in different environments absorb energy of different frequencies. NMR spectroscopy measures these differences relative to a standard substance — the difference is called the chemical shift (δ).

Chiral molecule
A molecule that contains a carbon atom with four different groups attached to it.

Chlorofluorocarbon (CFC)
A haloalkane containing fluorine and chlorine and no hydrogen. CFCs contribute to ozone depletion.

Chromatogram
A visual record (such as a pattern of spots or a graph) of the results of a chromatography experiment.

Chromatography
An analytical technique which is used to separate out mixtures.

***Cis-trans* isomerism**
A special type of *E*/*Z* isomerism where two of the groups attached to the carbon atoms around the C=C double bond are the same.

Citation
Details about where to find the source of a piece of information.

Clock reaction
A method used to find the initial rate of a reaction. In clock reactions you measure the time it takes for a given amount of product to form.

Closed system
A system where nothing can get in or out.

Collision theory
The theory that a reaction will not take place between two particles unless they collide in the right direction and with at least a certain minimum amount of kinetic energy.

Complete combustion
Burning a substance completely in an excess of oxygen. Complete combustion of a hydrocarbon will produce carbon dioxide and water only.

Complex ion
A metal ion surrounded by coordinately bonded ligands.

Concentration
A measure of how many moles (or how many grams) of a substance are dissolved in a volume of solution.

Condensation polymer
A type of polymer formed through a series of condensation reactions.

Condensation reaction
A reaction in which two molecules join together with the loss of a small molecule, such as water or hydrogen chloride. The opposite of a hydrolysis reaction.

Conjugate pair
A set of two species that can be transformed into each other by gaining or losing a proton.

Continuous data
Data that can have any value on a scale.

Continuous monitoring
A method used to monitor the progress of a reaction. The formation or loss of one of the substances in the reaction is measured at regular intervals over the entire course of the reaction, and the data is used to construct a concentration-time graph.

Coordinate bond
A covalent bond formed when one atom provides both of the shared electrons. Also called a dative covalent bond.

Coordination number
The number of coordinate bonds that are formed with the central metal ion in a complex ion.

Correlation
The relationship between two variables.

Corrosive substance
Something that may cause chemical burns.

Covalent bond
The strong electrostatic attraction between a shared pair of electrons and the nuclei of the bonded atoms.

Curly arrow
An arrow used in a reaction mechanism to show the movement of a pair of electrons.

Cycloalkane
A type of alkane which has one or more non-aromatic carbon rings.

D

d-block
The block of elements in the middle of the periodic table.

d-sub-shell
A type of sub-shell. Each can hold ten electrons.

Data logger
A piece of software on a tablet or computer that can record data readings as they are made and store them to be looked at later.

Dative covalent bond
A covalent bond formed when one atom provides both of the shared electrons. Also called a coordinate bond.

Dehydration reaction
A reaction in which water is eliminated from an organic molecule.

Delocalised electron
An electron that is not attached to a specific atom.

Dependent variable
The variable that you measure during an experiment.

Deuterated solvent
A solvent which has had all of its hydrogen atoms exchanged for deuterium atoms.

Deuterium
An isotope of hydrogen. It contains one neutron, one proton and one electron.

Dibasic acid
An acid that can release two H^+ ions per molecule.

Dipole
A difference in charge between two atoms caused by a shift in the electron density in a bond.

Discrete data
Data that can only take certain values.

Displacement reaction
A reaction where a more reactive element pushes out (displaces) a less reactive element from an ionic solution.

Displayed formula
A way of representing a molecule that shows how all the atoms are arranged, and all the bonds between them.

Disproportionation
When an element is both oxidised and reduced in a single chemical reaction.

Distillation
An organic technique used to heat a reaction mixture. Any products that have a boiling point lower than the temperature of the reaction mixture will condense out of the reaction mixture as soon as they form. They can then be collected in a separate vessel.

Drying agent
An anhydrous salt used to remove small amounts of water from an organic mixture. Drying agents include anhydrous magnesium sulfate ($MgSO_4$) and anhydrous calcium chloride ($CaCl_2$).

Dynamic equilibrium
In a reversible reaction, dynamic equilibrium is reached when the concentrations of reactants and products are constant, and the forwards reaction and the backwards reaction are going at the same rate.

E

***E/Z* isomerism**
A type of stereoisomerism that is caused by the restricted rotation about a carbon-carbon double bond. Each of the carbon atoms must be attached to two different groups.

Electric heater
A piece of equipment used to heat a chemical mixture, using a plate of metal that is heated to a set temperature.

Electrochemical cell
An electrical circuit made from two metal electrodes (which are connected by a wire) dipped in salt solutions (which are connected by a salt bridge).

Electrochemical series
A list of electrode potentials written in order from most negative to most positive.

Electrode potential
The voltage measured when a half-cell is connected to a standard hydrogen electrode.

Electromotive force (e.m.f.)
Another name for cell potential.

Electron
A subatomic particle with a relative charge of 1– and a relative mass of 1/2000, located in orbitals around the nucleus.

Electron configuration
The number of electrons that an atom or ion has and how they are arranged.

Electron shell
A region of an atom with a fixed energy that contains electrons orbiting the nucleus.

Electron shell repulsion theory
The theory that in a molecule lone pair/lone pair bond angles are the biggest, lone pair/bonding pair bond angles are the second biggest and bonding pair/bonding pair bond angles are the smallest.

Electron shielding
When inner electrons effectively screen the outer electrons from the pull of the nucleus.

Electronegativity
The ability of an atom to attract the bonding electrons in a covalent bond.

Electrophile
An electron-pair acceptor. It is an electron deficient (and usually positively charged) species which is attracted to regions of high electron density.

Electrophilic addition
A reaction mechanism where a double bond in an alkene opens up and atoms are added to the carbon atoms.

Electrophilic substitution
A reaction mechanism where an electrophile substitutes for another atom (usually a hydrogen) in a molecule.

Elimination reaction
A reaction where a functional group is lost from a molecule and released as a small molecule, such as a hydrogen halide or water.

Empirical formula
A formula giving the simplest whole number ratio of atoms of each element in a compound.

Enantiomer
A molecule that has the same structural formula as another molecule but is a non-superimposable mirror image of the other molecule.

End point
The point in a titration at which all the acid is just neutralised and the pH curve becomes vertical.

Endothermic reaction
A reaction that absorbs energy in the form of heat (ΔH is positive).

Enthalpy change
The heat energy transferred in a reaction at constant pressure (ΔH).

Enthalpy change of atomisation of a compound ($\Delta_{at} H$)
The enthalpy change when 1 mole of a compound is converted to gaseous atoms.

Enthalpy change of atomisation of an element ($\Delta_{at} H$)
The enthalpy change when 1 mole of gaseous atoms is formed from an element.

Enthalpy change of formation ($\Delta_f H$)
The enthalpy change when 1 mole of a compound is formed from its elements.

Enthalpy change of hydration ($\Delta_{hyd} H$)
The enthalpy change when 1 mole of gaseous ions is dissolved in water.

Enthalpy change of solution ($\Delta_{sol} H$)
The enthalpy change when 1 mole of solute is dissolved in a solvent.

Enthalpy profile diagram
A graph showing how the enthalpy changes during a chemical reaction.

Entropy (S)
A measure of the dispersal of energy in a system (e.g. the number of ways that particles can be arranged and the number of ways that the energy can be shared out between the particles).

Equilibrium constant (K_c)
A ratio worked out from the concentration of the products and reactants once a reversible reaction has reached equilibrium.

Ester
A molecule that contains the functional group RCOOR.

Ester link
The -COO- group which is found between monomers in a polyester.

Esterification
Forming an ester by heating a carboxylic acid and an alcohol in the presence of a strong acid catalyst (or by reacting an acid anhydride with an alcohol).

Exothermic reaction
A reaction that gives out energy in the form of heat (ΔH is negative).

F

False positive	A result that suggests the presence of something (e.g. ions) that isn't actually there.
Feasible reaction	A reaction which has a free energy change that is less than or equal to zero and can happen by itself without energy being supplied.
Filtration	A technique used to separate solids from liquids.
Filtration under reduced pressure	A technique for removing liquid impurities from an organic solid.
First electron affinity	The energy needed to change 1 mole of gaseous atoms into 1 mole of gaseous 1– ions.
First ionisation energy	The energy needed to change 1 mole of gaseous atoms into 1 mole of gaseous 1+ ions.
Flammable	A substance that will easily catch fire.
Free energy change (ΔG)	A measure which links enthalpy and entropy changes to predict whether a reaction is feasible. $\Delta G = \Delta H - T\Delta S$
Fuel cell	A device that converts the energy of a fuel into electricity through an oxidation reaction.
Functional group	The group of atoms within a molecule that is responsible for the characteristic reactions of a molecule (e.g. –OH for alcohols, –COOH for carboxylic acids, C=C for alkenes).
Functional group isomer	A molecule that has the same molecular formula as another molecule, but with the atoms arranged into different functional groups.

G

Gas chromatography (GC)	A type of chromatography where the sample is carried in a stream of gas through a coiled tube, coated with a viscous liquid (such as an oil) or a solid.
Gas equilibrium constant (K_p)	A ratio worked out from the partial pressures of the gaseous products and reactants once a reversible reaction has reached equilibrium.
General formula	An algebraic formula that can describe any member of a homologous series of compounds.
Giant covalent lattice	A structure consisting of a huge network of covalently bonded atoms. Also called a macromolecular structure.
Giant ionic lattice structure	A regular repeated structure made up of oppositely charged ions strongly attracted to each other in all directions.
Giant metallic lattice structure	A regular structure consisting of closely packed positive metal ions in a sea of delocalised electrons.
Global warming	The warming of the planet due to increased concentrations of greenhouse gases in the troposphere, which enhance the greenhouse effect.
Gradient	The steepness of a line.
Greenhouse effect	The absorption and re-emission of infrared radiation by greenhouse gases in the troposphere.
Greenhouse gas	A gas that absorbs and emits infrared radiation and so contributes to the greenhouse effect.
Group	A column in the periodic table.

H

Haemoglobin	A protein found in blood that helps to transport oxygen around the body.
Half-cell	One half of an electrochemical cell.
Half-equation	An equation that shows oxidation or reduction — one half of a full redox equation.
Half-life	The time it takes for half of the reactant to be used up during a reaction.
Halide	A negative ion of a halogen.
Haloalkane	An alkane with at least one halogen atom in place of a hydrogen atom.
Halogen	An element in Group 7 of the periodic table.
Halogen carrier	A molecule which can accept a halogen atom (e.g. $AlCl_3$). Used as a catalyst in the halogenation of benzene, and also in Friedel-Crafts acylation and alkylation.
Hess's law	The total enthalpy change of a reaction is always the same, no matter which route is taken.
Heterogeneous catalyst	A catalyst which is in a different physical state from the reactants of the reaction it's catalysing.
Heterogeneous equilibrium	An equilibrium mixture where the reactants and products are in different states.
Heterolytic fission	When a covalent bond breaks unevenly, with one of the bonding atoms receiving both of the electrons from the bonded pair, resulting in the formation of a positively charged cation and a negatively charged anion.
Homogeneous catalyst	A catalyst which is in the same physical state as the reactants of the reaction it's catalysing.

Homogeneous equilibrium
An equilibrium mixture where the reactants and products are in the same state.

Homologous series
A family of organic compounds that have the same general formula and similar chemical properties.

Homolytic fission
When a covalent bond breaks evenly, with each bonding atom receiving one electron from the bonded pair, resulting in the formation of two electrically uncharged radicals.

Hydrated salt
A salt that contains water of crystallisation.

Hydrocarbon
A molecule that only contains hydrogen and carbon atoms.

Hydrogen bond
The strongest intermolecular force. It occurs when polarised covalent bonds cause hydrogen atoms to form weak bonds with lone pairs of electrons on the fluorine, nitrogen or oxygen atoms of other molecules.

Hydrolysis reaction
A reaction where molecules are split apart by water molecules. The water molecules are also split into hydrogen ions (H^+) and hydroxide ions (OH^-). The opposite of a condensation reaction.

Hydroxynitrile
An organic compound containing a $-C{\equiv}N$ and an $-OH$ functional group.

I

Incomplete combustion
Burning a substance in a poor supply of oxygen. Incomplete combustion of a hydrocarbon produces carbon monoxide, water and sometimes carbon and carbon dioxide.

Independent variable
The variable that you change during an experiment.

Indicator
A substance that changes colour over a particular pH range.

Induced dipole-dipole interactions
A type of intermolecular force caused by temporary dipoles, which causes all atoms and molecules to be attracted to each other. Also called London (dispersion) forces.

Infrared (IR) spectroscopy
An analytical technique used to identify the functional groups present in a molecule, by measuring the infrared absorption frequencies of its bonds.

Initial rates method
An experimental technique used to work out the initial rate of a reaction by timing how long it takes for a set amount of product to form or reactant to be used. This data can be used to work out the order of reaction with respect to each reactant.

Integration trace
A line on a proton NMR spectrum that has a change in height that is proportional to the area of the peak it's next to.

Intermolecular forces
Forces between molecules, e.g. induced dipole-dipole forces, permanent dipole-dipole forces and hydrogen bonding.

Ion
A charged particle formed when one or more electrons are lost or gained by an atom or molecule.

Ionic bond
An electrostatic attraction between positive and negative ions.

Ionic equation
An equation which only shows the reacting particles of a reaction involving ions.

Ionic product of water
An equilibrium constant specific to water that describes the dissociation of water at a constant temperature.
$K_w = [H^+][OH^-]$

Ionisation
The removal of one or more electrons from an atom or molecule, resulting in an ion forming.

Irritant
A substance that may cause inflammation or discomfort.

Isotope
One of two or more forms of an element with the same number of protons but different numbers of neutrons and masses.

Isotopic abundance
The relative amount of a particular isotope occurring in a sample of an element.

K

Ketone
A substance with the general formula $C_nH_{2n}O$ which has two alkyl groups attached to the carbonyl carbon atom.

L

Lattice
A regular structure made up of atoms or ions.

Lattice enthalpy ($\Delta_{LE}H$)
The enthalpy change when 1 mole of a solid ionic compound is formed from its gaseous ions.

Le Chatelier's principle
If there's a change in concentration, pressure or temperature, the equilibrium will move to help counteract the change.

Ligand
An atom, ion or molecule that donates a pair of electrons to a central metal ion in a complex ion.

Ligand substitution reaction
A reaction where one or more ligands are changed for one or more other ligands in a complex ion. (Also called a ligand exchange reaction.)

Logarithmic constant (pK_a)
The logarithmic form of the acid dissociation constant, K_a.
$pK_a = -\log_{10} K_a$

M

Macromolecular structure
A structure consisting of a huge network of covalently bonded atoms. Also called a giant covalent lattice.

Mass number
The total number of protons and neutrons in the nucleus of an atom.

Mass spectrometry
An analytical technique used to find the structure of a molecule by measuring the masses of the ions it produces when it's bombarded with electrons.

Mass spectrum
A chart produced by a mass spectrometer.

Melting point determination
A technique for determining the purity of an organic solid. The melting point of the sample solid is compared to the standard melting point of the pure solid. The closer the agreement between the two values, the more pure the sample is.

Methyl orange
A pH indicator that changes colour between pH 3.1 and 4.4.

Model
A simplified picture or representation of a real physical situation.

Molar mass
The mass of one mole of something.

Molar ratio
The ratio of the number of moles of each reactant and product in a balanced chemical equation.

Mole
The unit of amount of substance. One mole is roughly 6.02×10^{23} particles (the Avogadro constant).

Mole fraction
The proportion of a gas mixture that is made up of a particular gas.

Molecular formula
A way of representing molecules that shows the actual number of atoms of each element in a molecule.

Molecular ion
An ion made up of a group of atoms with an overall charge.

Monobasic acid
An acid that releases one H^+ ion per molecule. (Also known as a monoprotic acid.)

Monodentate ligand
A ligand that can only form one coordinate bond. (Also known as a unidentate ligand.)

Monomer
A small molecule which can join together with other monomers to form a polymer.

Multidentate ligand
A ligand that can form three or more coordinate bonds.

Multiplet
A split peak on a proton spectrum. (General term for a doublet, triplet, quartet, quintet etc.)

N

$n + 1$ rule
Peaks on a proton NMR spectrum always split into the number of non-equivalent hydrogens on the neighbouring carbon, plus one.

Neutralisation reaction
A reaction between an acid and a base to produce a salt and water.

Neutron
A subatomic particle with a charge of 0 and a relative mass of 1, located in the nucleus of an atom.

Nitration
A reaction in which a nitro group ($-NO_2$) is added to a molecule.

Nitrile
An organic compound containing a $-C\equiv N$ functional group.

Noble gas
An element in Group 0 of the periodic table. These elements are extremely stable because they have a full outer electron shell.

Nomenclature
A fancy word for naming organic compounds.

Nuclear magnetic resonance (NMR) spectroscopy
An analytical technique which uses the absorption of low-energy radio waves to determine the relative environment of an atom within a compound.

Nuclear model of the atom
A model for the structure of an atom proposed by Rutherford.
He suggested that atoms consist of a small positively charged nucleus surrounded by a cloud of negatively charged electrons.

Nucleophile
An electron-pair donor. Nucleophiles are electron rich, so they are attracted to areas of positive charge.

Nucleophilic addition
A reaction mechanism where a nucleophile adds on to the δ^+ carbon atom of a carbonyl group.

Nucleophilic substitution reaction
A reaction where a nucleophile attacks a polar molecule and replaces a functional group in that molecule.

Nucleus
The central part of an atom or ion, made up of protons and neutrons.

O

Optical isomer
A molecule that has the same structural formula as another molecule but is a non-superimposable mirror image of the other molecule.

Orbital
A region of a sub-shell that contains a maximum of 2 electrons with opposite spins.

Ordered / ordinal data
Categoric data where the categories can be put in order.

Overall order (of reaction)
The sum of the orders of each reactant in a reaction.

Oxidation
Loss of electrons.

Oxidation number
The total number of electrons an element has donated or accepted. Also called an oxidation state.

Oxidation state
The total number of electrons an element has donated or accepted. Also called an oxidation number.

Oxidising agent
Something that accepts electrons and gets reduced.

P

Paper chromatography
A technique for testing the purity of an organic mixture. The mixture is separated into its component parts by a solvent moving up a plate made of paper.

Partial pressure
The pressure exerted by an individual gas in a mixture of gases.

Peer review
The evaluation of a scientific report by other scientists who are experts in the same area (peers). They go through it bit by bit, examining the methods and data, and checking it's all clear and logical.

Percentage yield
The amount of product that is actually obtained during a reaction expressed as a percentage of the amount of product that should form.

Period
A row in the periodic table.

Periodic table
A table of the elements arranged in order of increasing atomic number and organised into periods and groups.

Periodicity
The trends in physical and chemical properties of elements as you go across the periodic table.

Permanent dipole-dipole interactions
Intermolecular forces that exist because the difference in electronegativities in a polar bond causes weak electrostatic forces of attraction between molecules.

pH
A measure of the hydrogen ion concentration in a solution.
$\text{pH} = -\log_{10}[\text{H}^+]$

pH chart
A chart to show the colour of an indicator at different pHs.

pH curve
A graph used to follow the progress of an acid-base titration. You make a pH curve by plotting the pH against the volume of acid (or alkali) added.

pH meter
An electronic gadget used to measure pH, made up of a probe connected to a digital display.

Phenol
An aromatic organic compound with the formula C_6H_5OH.

Phenolphthalein
A pH indicator that changes colour between pH 8.3 and 10.

Pi (π-) bond
A type of bond formed when two p orbitals overlap sideways.

Plane polarised light
Light where the waves all vibrate in the same direction.

Plum pudding model
A model for the structure of an atom proposed by Thomson. He suggested that atoms consist of a positively charged sphere with negatively charged electrons embedded in them.

Polar bond
A covalent bond where a difference in electronegativity has caused a shift in electron density in the bond.

Polar molecule
A molecule containing polar bonds that are arranged so that the dipoles don't cancel each other out, causing an overall dipole to be created across the molecule.

Polyamide
A polymer that has amide links between the monomers.

Polyester
A polymer that has ester links between the monomers.

Polymer
A long molecule formed from lots of repeating units (called monomers).

Polymerisation
The process of forming a polymer from monomers.

Positional isomer
A molecule with the same molecular formula as another molecule but with the functional group in a different position.

Precipitate
A solid that forms in a solution.

Precise result
A result that can be consistently reproduced in independent experiments.

Proton
A subatomic particle with a relative charge of 1+ and a relative mass of 1, located in the nucleus of an atom.

Proton (atomic) number
The number of protons in the nucleus of an atom.

Q

Quantum model
The currently accepted model for the structure of an atom, where particles' positions are predicted by probabilities.

R

Radical
A particle with an unpaired electron, written like this — Cl• or CH_3•.

Random error
The uncertainty in a measurement that results from random variations between repeated tests.

Rate constant (*k*)
A constant in the rate equation. The larger it is, the faster the rate of reaction.

Rate-determining step
The slowest step in a reaction mechanism which determines the overall rate of a reaction.

Rate equation
An equation of the form $\text{rate} = k[A]^m[B]^n$ which tells you how the rate of a reaction is affected by the concentration of the reactants.

Reaction order
A number that tells you how the concentration of a particular reactant affects the reaction rate.

Reaction rate
The change in the amount of reactants or products per unit time.

Recrystallisation
A technique used to purify an organic solid. The solid is dissolved in a minimal amount of a hot solvent, and then the solution is cooled. As the solution cools, the pure solid becomes insoluble in the solvent and crystallises out.

Redistillation
A technique to purify a mixture of liquids that all have different boiling points. A mixture is gently heated so that substances evaporate and can be collected in order of increasing boiling point.

Redox potential
The voltage measured when a half-cell is connected to a standard hydrogen electrode.

Redox reaction
A reaction where reduction and oxidation happen simultaneously.

Redox titration
A titration that can be performed to determine how much reducing agent is needed to exactly react with a known quantity of oxidising agent, or vice versa.

Reducing agent
Something that donates electrons and gets oxidised.

Reduction
Gain of electrons.

Reflux
An organic technique where a mixture is heated in such a way that volatile compounds can't evaporate from the reaction apparatus, but instead condense and fall back into the mixture.

Relative atomic mass
The average mass of an atom of an element compared to 1/12 of the mass of an atom of carbon-12.

Relative formula mass
The average mass of a molecule or formula unit compared to 1/12 of the mass of an atom of carbon-12.

Relative isotopic mass
The mass of an atom of an isotope of an element compared to 1/12 of the mass of an atom of carbon-12.

Relative molecular mass
The average mass of a molecule compared to 1/12 of the mass of an atom of carbon-12.

Repeat unit
A part of a polymer that repeats over and over again.

Retention time
The time taken from the injection of a sample to the moment when a substance is detected in gas chromatography.

R_f value
The ratio of the distance travelled by a spot to the distance travelled by the solvent in thin-layer chromatography.

S

Salt
A compound formed when the hydrogen in an acid molecule is replaced by a metal ion or ammonium ion.

Salt bridge
A connection between two half-cells that ions can flow through, used to complete the circuit in an electrochemical cell. Often a piece of filter paper soaked in a salt solution.

Sand bath
A piece of equipment used to heat a chemical mixture. Made up of a container filled with sand that can be heated to a set temperature. The vessel containing the reaction mixture is submerged in the sand and so is heated.

Saturated hydrocarbon
A hydrocarbon where all the carbon-carbon bonds are single bonds.

Second electron affinity
The energy needed to change 1 mole of gaseous 1– ions into 1 mole of gaseous 2– ions.

Second ionisation energy
The energy needed to change 1 mole of gaseous 1+ ions into 1 mole of gaseous 2+ ions.

Separation
A technique to separate the water-soluble impurities out of an organic mixture. The aqueous and organic solutions can be separated as they are immiscible, and separate out into two distinct layers due to their different densities.

Sigma (σ-) bond
A type of bond formed when two orbitals overlap directly between the bonded atoms.

Silver nitrate test
A test that uses silver nitrate to identify halide ions in a solution.

Simple molecular structure
A compound with strong covalent bonds within its molecules but weak forces between its molecules.

Skeletal formula
A simplified organic formula which only shows the carbon skeleton and associated functional groups.

Specific heat capacity
The amount of heat energy it takes to raise the temperature of 1 g of a given substance by 1 K.

Spin
A type of momentum possessed by an electron. Spin can either be 'down' or 'up'.

Splitting pattern
Peaks on proton NMR spectra may be split into further peaks. The resultant group of peaks is called a splitting pattern.

Standard conditions
A temperature of 298 K (25 °C), a pressure of 100 kPa and all ion solutions having a concentration of 1.00 mol dm^{-3}.

Standard electrode potential
The voltage measured under standard conditions when a half-cell is connected to a standard hydrogen electrode.

Standard enthalpy change of combustion
The enthalpy change when 1 mole of a substance is completely burned in oxygen under standard conditions with all reactants and products in their standard states ($\Delta_c H^{\ominus}$).

Standard enthalpy change of formation
The enthalpy change when 1 mole of a compound is formed from its elements in their standard states under standard conditions ($\Delta_f H^{\ominus}$).

Standard enthalpy change of neutralisation
The enthalpy change when an acid and an alkali react together to form 1 mole of water, under standard conditions ($\Delta_{neut} H^{\ominus}$).

Standard enthalpy change of reaction
The enthalpy change when a reaction occurs in the molar quantities shown in the chemical equation, under standard conditions ($\Delta_r H^{\ominus}$).

Standard hydrogen electrode
An electrode where hydrogen gas is bubbled through a solution of aqueous H^+ ions under standard conditions.

Standard redox potential
The voltage measured under standard conditions when a half-cell is connected to a standard hydrogen electrode.

Standard solution
A solution with a precisely known concentration.

Standard state
A substance's physical state under standard conditions (100 kPa and 298 K).

State symbol
A symbol placed after a chemical in an equation that tells you what state of matter it is in.

Stereoisomer
A molecule that has the same structural formula as another molecule but with the atoms arranged differently in space.

Strong acid/base
An acid or base that dissociates almost fully in water.

Structural formula
A way of representing molecules that shows the atoms carbon by carbon, with the attached hydrogens and functional groups.

Structural isomer
A molecule with the same molecular formula as another molecule, but with the atoms connected in a different way.

Sub-shell
A sub-division of an energy level (shell). Sub-shells may be s, p, d or f sub-shells.

Substitution reaction
A reaction in which one functional group is swapped for another.

Successive ionisation energy
The energy needed to remove 1 mole of each subsequent electron from each ion in 1 mole of positively charged gaseous ions.

Synthesis
A method detailing how to create a chemical.

Synthetic route
A step-by-step pathway of how to get from one organic compound to another, showing the reagents, catalysts and conditions needed, as well as any intermediate products.

Systematic error
An error in a measurement that happens every time you repeat an experiment. It may be caused by the set-up or the piece of equipment that has been used.

T

Tangent
A line that just touches a curve and has the same gradient as the curve does at that point.

Theoretical yield
The mass of product that should be formed in a chemical reaction, if no reactant or product is 'lost'.

Thin-layer chromatography (TLC)
A type of chromatography where a solvent moves over a glass or plastic plate, which is covered in a thin layer of solid, resulting in the separation of a mixture of substances.

Titration
An analytical technique used to calculate the concentration of a species in solution. It involves gradually adding one solution to a known volume of another until the reaction between the two is complete.

Tollens' reagent
A colourless solution of silver nitrate dissolved in aqueous ammonia which can be used to distinguish between aldehydes and ketones.

Toxic substance
A substance that can cause illness or even death.

Transition element
A metal that can form one or more stable ions with a partially filled d-sub-shell.

Tribasic acid
An acid that can release three H^+ ions per molecule.

U

Unsaturated hydrocarbon
A hydrocarbon with one or more carbon-carbon double bonds, carbon-carbon triple bonds or an aromatic group.

V

Valid result
A result which answers the question it was intended to answer.

Variable
A quantity that has the potential to change.

Volatility
A substance's tendency to evaporate (turn into a gas).

W

Water bath
A piece of equipment used to heat a chemical mixture. Made up of a container filled with water that can be heated to a set temperature. The vessel containing the reaction mixture is submerged in the water and so is heated.

Water of crystallisation
The water contained in an ionic lattice.

Weak acid/base
An acid or base that only partially dissociates in water.

Y

Yield
The amount of product you get from a reaction.

IR Data

Bond	Where it's found	Wavenumber (cm^{-1})
C–C	alkanes, alkyl chains	750 – 1100
C–X	haloalkanes (X = Cl, Br, I)	500 – 800
C–F	fluoroalkanes	1000 – 1350
C–O	alcohols, esters, carboxylic acids	1000 – 1300
C=C	alkenes	1620 – 1680
C=O	aldehydes, ketones, carboxylic acids, esters, amides, acyl chlorides, acid anhydrides	1630 – 1820
aromatic C=C	arenes	several peaks in range 1450 – 1650 (variable)
C≡N	nitriles	2220 – 2260
C–H	most organic molecules	2850 – 3100
O–H	carboxylic acids	2500 – 3300 (broad)
N–H	amines, amides	3300 – 3500
O–H	alcohols, phenols	3200 – 3600

Acknowledgements

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Graph to show trend in atmospheric CO_2 concentration and global temperature on page 262 based on data by EPICA Community Members 2004 and Siegenthaler et al 2005.

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The Periodic Table

Periods	Group 1	Group 2											Group 3	Group 4	Group 5	Group 6	Group 7	Group 0
1								1.0 H Hydrogen 1										4.0 He Helium 2
2	6.9 Li Lithium 3	9.0 Be Beryllium 4											10.8 B Boron 5	12.0 C Carbon 6	14.0 N Nitrogen 7	16.0 O Oxygen 8	19.0 F Fluorine 9	20.2 Ne Neon 10
3	23.0 Na Sodium 11	24.3 Mg Magnesium 12											27.0 Al Aluminium 13	28.1 Si Silicon 14	31.0 P Phosphorus 15	32.1 S Sulfur 16	35.5 Cl Chlorine 17	39.9 Ar Argon 18
4	39.1 K Potassium 19	40.1 Ca Calcium 20	45.0 Sc Scandium 21	47.9 Ti Titanium 22	50.9 V Vanadium 23	52.0 Cr Chromium 24	54.9 Mn Manganese 25	55.8 Fe Iron 26	58.9 Co Cobalt 27	58.7 Ni Nickel 28	63.5 Cu Copper 29	65.4 Zn Zinc 30	69.7 Ga Gallium 31	72.6 Ge Germanium 32	74.9 As Arsenic 33	79.0 Se Selenium 34	79.9 Br Bromine 35	83.8 Kr Krypton 36
5	85.5 Rb Rubidium 37	87.6 Sr Strontium 38	88.9 Y Yttrium 39	91.2 Zr Zirconium 40	92.9 Nb Niobium 41	95.9 Mo Molybdenum 42	98 Tc Technetium 43	101.1 Ru Ruthenium 44	102.9 Rh Rhodium 45	106.4 Pd Palladium 46	107.9 Ag Silver 47	112.4 Cd Cadmium 48	114.8 In Indium 49	118.7 Sn Tin 50	121.8 Sb Antimony 51	127.6 Te Tellurium 52	126.9 I Iodine 53	131.3 Xe Xenon 54
6	132.9 Cs Caesium 55	137.3 Ba Barium 56	138.9 La Lanthanum 57	178.5 Hf Hafnium 72	180.9 Ta Tantalum 73	183.8 W Tungsten 74	186.2 Re Rhenium 75	190.2 Os Osmium 76	192.2 Ir Iridium 77	195.1 Pt Platinum 78	197.0 Au Gold 79	200.6 Hg Mercury 80	204.4 Tl Thallium 81	207.2 Pb Lead 82	209.0 Bi Bismuth 83	209 Po Polonium 84	210 At Astatine 85	222 Rn Radon 86
7	223 Fr Francium 87	226.0 Ra Radium 88	Ac Actinium 89	Rf Rutherfordium 104	Db Dubnium 105	Sg Seaborgium 106	Bh Bohrium 107	Hs Hassium 108	Mt Meitnerium 109	Ds Darmstadtium 110	Rg Roentgenium 111	Cn Copernicium 112		Fl Flerovium 114		Lv Livermorium 116		

Relative Atomic Mass (A_r) →

Atomic (proton) number →

The Lanthanides	140.1 Ce Cerium 58	140.9 Pr Praseodymium 59	144.2 Nd Neodymium 60	144.9 Pm Promethium 61	150.4 Sm Samarium 62	152.0 Eu Europium 63	157.2 Gd Gadolinium 64	158.9 Tb Terbium 65	162.5 Dy Dysprosium 66	164.9 Ho Holmium 67	167.3 Er Erbium 68	168.9 Tm Thulium 69	173.0 Yb Ytterbium 70	175.0 Lu Lutetium 71
The Actinides	232.0 Th Thorium 90	Pa Protactinium 91	238.1 U Uranium 92	Np Neptunium 93	Pu Plutonium 94	Am Americium 95	Cm Curium 96	Bk Berkelium 97	Cf Californium 98	Es Einsteinium 99	Fm Fermium 100	Md Mendelevium 101	No Nobelium 102	Lr Lawrencium 103

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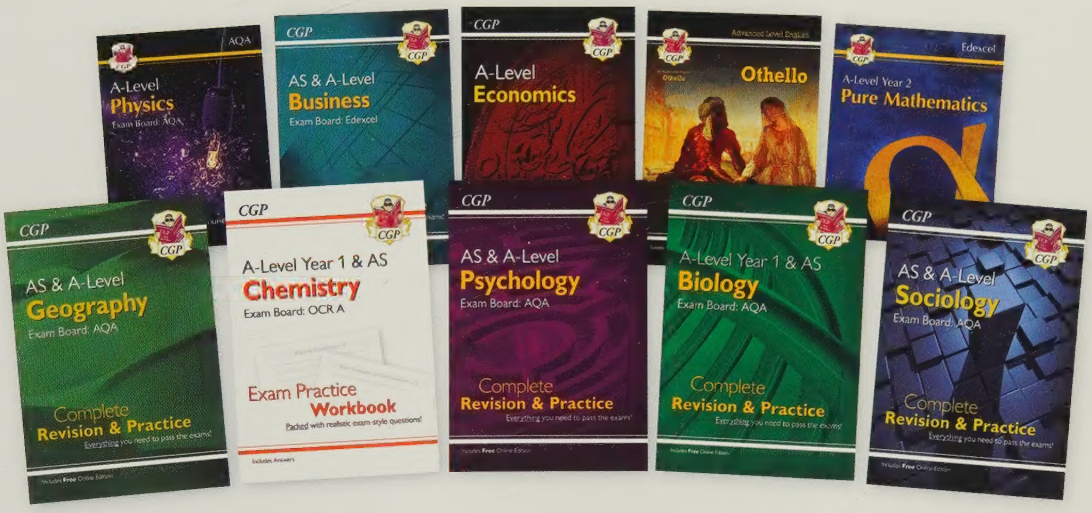
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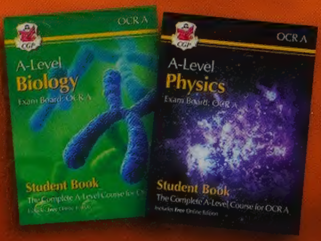
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